

SPATIAL MODELS OF MOLECULES IN CHEMICAL RESEARCH AND IN TUITION, II

By

K. TETTAMANTI and J. TÖRÖK

Department of Unit Operations, Polytechnical University, Budapest

(Received December 18, 1967)

III. DESCRIPTION OF A NOVEL TYPE OF ATOMIC CALOTTE MODEL WITH TRUE ANGLES (EUGON)

I. General description

In what follows, a general description is given of the *Eugon atom-calotte models* designed in Hungary in the years 1955 to 1958, and marketed in 1967.

The utilization of the most reliable data available for van der Waals radii (r), bond radii (R), and bond angles has been our practice in the design of these models. It is principally by the adoption of correct angles that the *Eugon* models differ from known constructions, a further difference is the realization of all the important types of bonds for the eleven elements comprised in the set (cf. Table IV).

Table IV

Elements involved in bonding	Number of bond types for the element
1. Carbon	6
2. Hydrogen	2
3. Oxygen	3
4. Nitrogen	11
5—8. Halogens	4
9. Phosphorus	2
10. Sulphur	4
11. Silicium	1
altogether	33 types of bonding

The *Eugon* atom-calotte models are moulded from phenoplast, and aminoplast powders.*

The models truly represent real dimensions in a scale of 1 : 10⁸, viz. one centimetre measured on a model is 1 Å in fact.

* Here we wish to thank Messrs *Montecatini*, of Italy, for having made their GABRIT moulding powders, in various colours, available.

Table V
Eugon atomic

Cat. No.	Atom species	Bond arrangement	Bond angle	van der Waals radii, Å $r_T^*(r_{T,corr})$
1.	C-paraffinic (tetrahedral)		$\alpha = \beta = \gamma = \delta = 109.5$	1.30
2.	C-olefinic		$\alpha = \beta = \gamma = 120^\circ$	1.30
21.	C-carbonyl in carboxylic group		$\alpha = 112^\circ$ $\beta = \gamma = 124^\circ$	1.30
3.	C-aromatic in benzene		$\alpha = \beta = \gamma = 120^\circ$	1.30
4.	C-acetylene	$-C \equiv$	180°	1.30
5.	C-allene	$=C =$	180°	1.30
6.	C-aromatic-5 ring		$\alpha = 108 - 112.5^\circ$ $\beta = 130 - 127.5^\circ$ $\gamma = 120^\circ$	1.30
61.	C-saturated in cyclopentadiene		$\alpha = 101^\circ$	1.30
7.	Hydrogen	H—	—	0.95
8.	H-bond	...H—	—	0.50
9.	O-single bond		$105^\circ (109^\circ)$	1.23
91.	O-furane		107°	1.23
92.	O-pyrone		dioxine: 120°	1.23
10.	O-double bond O-carbonyl	O=	—	1.23
101.	O-negative	O...	—	1.23

models

Covalent radii, Å				Colour; note
R_0	$R_{\sigma\pi}$	$R_{\sigma\pi\pi}$	$R_{\sigma p\pi}$	
0.77	—	—	—	Black
0.77	0.665	—	—	Black
0.77	0.665	—	—	No in set, use No. 2
0.77	—	—	0.695	Black
0.75	—	0.605	—	Black
—	0.665	—	—	Black
C: 0.725 H: 0.77	0.675	—	—	Black
C: 0.80 H: 0.77	—	—	—	No in set, use No. 1
0.30	—	—	—	White
0.30	—	—	—	White
0.66	—	—	—	Red
0.68	—	—	—	No in set, use No. 9
0.64	—	—	—	No in set, use No. 9 (Data are not available)
—	0.55	—	—	Red
—	—	—	0.50	Red






Table V

Cat. No.	Atom species	Bond arrangement	Bond angle	van der Waals radii, Å $r_T^*(r_{T,corr})$
102.	O-oxonium		?	1.23
11.	N-amino		$\alpha = \beta = \gamma = 109.5^\circ$	1.311
12.	N-amide		$\alpha = \beta = \gamma = 120^\circ$	1.311
121.	N-nitro		$\alpha = 127^\circ$ $\beta = \gamma = 116.5^\circ$	1.311
13.	N-azo		120°	1.311
14.	N-aromatic-6 (quaterner pyridinium)		$\alpha = \beta = \gamma = 120^\circ$	1.40
141.	N-aromatic-6 (pyridine)		120°	1.40
15.	N-nitrile	$N \equiv$	—	1.40 (1.311)
16.	N-azide	$\dots N \equiv$	180°	1.278
17.	N-pyrrol (N-imide in 5-ring)		$\alpha = 105$ $\beta = \gamma = 127.5^\circ$	1.40
171.	N-pyrazole (N-azo in 5-ring)	$-N \equiv$?(108—112.5)?	1.40 (1.30)
18.	N-tetrahedral (quaterner)		$\alpha = \beta = \gamma = \delta = 109.5^\circ$	1.40 (1.311)
19.	Fluorine	F—	—	1.30 (1.253)
20.	Chlorine	Cl—	—	1.55 (1.486)
21.	Bromine	Br—	—	1.75 (1.635)
22.	Jodine	J—	—	1.90 (1.785)
23.	S-di-univalent		100°	1.47
24.	S-double bond (S-thiocarbonyl)	S=	—	1.47

cont.

Covalent radii, Å				Colour; note
R_{σ}	$R_{s,\pi}$	$R_{i,\pi\pi}$	$R_{s,p\pi}$	
?	—	—	?	No in set (Data are not available)
0.70	—	—	—	Blue
0.70	—	—	0.53	Blue
0.70	—	—	0.65	Blue
0.70	0.60	—	—	Blue
0.70	—	—	0.675	Blue
—	—	—	0.675	Blue
—	—	0.547	—	Blue
—	0.64	0.547	—	Blue
C: 0.70 H: 0.70	—	—	—	Blue
(0.725)	(0.675)	—	—	Blue The same as the No. 6 (Data are not available)
0.70	—	—	—	Blue
0.64	—	—	—	Light green
0.99	—	—	—	Green
1.14	—	—	—	Brown
1.33	—	—	—	Violet
1.04	—	—	—	Yellow
—	0.94	—	—	Yellow

Table V

Cat. No.	Atom species	Bond arrangement	Bond angle	van der Waals radii, Å $r_T^*(r_{T\text{-corr}})$
25.	S-thiophene		91°	1.47
26.	S-tetrahedral (S-sulfo)		109.5°	1.47
27.	Phosphorus		109.5°	1.518
28.	P-tervalent		109.5°	1.518
29.	Si-tetrahedral		109.5°	1.691

Tolerances are within ± 0.05 cm, and $\pm 0.5^\circ$.

All the dimensional data of a set of *Eugon* atom calottes are listed in Table V.

2. The van der Waals radii of the *Eugon* models

These models follow Stuart's school in so far as they have r_T^* data calculated for $T = 300^\circ \text{K}$ as the basis of their dimensions. The designation r^* (STUART), or r' (BRIEGLEB) indicates that van der Waals radii are not deduced from gas-kinetical data (r) of the element molecules, but are values (r_T^*) calculated, for room temperature, from partial constants of atoms involved in polar-covalent bonding within more complex organic molecules.

As for the numerical values r_T^* , the process used was the following.

1. In the case of C, H, O, N, F, Cl, Br and I, the data published by BRIEGLEB [5] in 1950 were accepted as the basis.

2. In the case of S, P and Si, no reliable data could be found in the literature, thus these were approached by analogy in the usual way.

a) It was assumed that for the first two rows of the periodic system

$$\frac{(r_T^*)_{\text{Phos}}}{(r_T^*)_{\text{Nitr}}} = \frac{(r_T^*)_{\text{Sulph}}}{(r_T^*)_{\text{Ox}}} = \frac{(r_T^*)_{\text{Chl}}}{(r_T^*)_{\text{Fl}}} = \frac{1.55}{1.30} = 1.19 \text{ holds,}$$

thus $(r_T^*)_{\text{Phos}} = 1.67$, and $(r_T^*)_{\text{Sulph}} = 1.47$. Since the value $(r_T^*)_{\text{Carbon}}$ is doubtful, no similar relationship for Si can be written.

b) It is legitimate to assume further that

$$\frac{(r_T^*)_{\text{Phos}}}{(r_{\text{min}}^*)_{\text{Phos}}} = \frac{(r_T^*)_{\text{Nitr}}}{(r_{\text{min}}^*)_{\text{Nitr}}} = \frac{1.40}{1.60} = 0.87, \text{ and that}$$

cont.

Covalent radii, Å				Colour; note
R_{σ}	$R_{\sigma\pi}$	$R_{\sigma\pi\pi}$	$R_{\sigma p\pi}$	
1.02	—	—	—	Yellow
1.04	—	—	0.94	Yellow
1.10	1.00	—	—	Orange
1.10	—	—	—	Orange
1.17	—	—	—	Grey

$$\frac{(r_T^*)_{\text{Sulph}}}{(r_{\min}^*)_{\text{Sulph}}} = \frac{(r_T^*)_{\text{Ox}}}{(r_{\min}^*)_{\text{Ox}}} = \frac{1.23}{1.40} = 0.88$$

On the basis of data given later by BRIEGLER [5b] $(r_{\min}^*)_{\text{Phos}} = 1.85$, and $(r_{\min}^*)_{\text{Sulph}} = 1.70$, thus $(r_T^*)_{\text{Phos}} = 1.61$, and $(r_T^*)_{\text{Sulph}} = 1.50$. If the factor 0.87–0.88 is accepted also for Si, then, according to [5b]: $(r_{\min}^*)_{\text{Si}} = 2.0$, $(r_T^*)_{\text{Si}} = 1.75$.

c) On the basis of data made available up to now the supposition is allowed that, for atoms of the same order of magnitude, $\frac{r_T^*}{r_{\min}^*} = \text{idem}$, i.e.

$$\frac{r_T^*_{\text{Phos}}}{r_{\min}^*_{\text{Phos}}} = \frac{r_T^*_{\text{Sulph}}}{r_{\min}^*_{\text{Sulph}}} = \frac{r_T^*_{\text{Chl}}}{r_{\min}^*_{\text{Chl}}} = \frac{1.55}{1.80} = 0.86$$

but $\frac{r_T^*_{\text{Si}}}{r_{\min}^*_{\text{Si}}} = \frac{r_T^*_{\text{I}_0}}{r_{\min}^*_{\text{I}_0}} = \frac{1.90}{2.05} = 0.925$

since, however [5b], $r_{\min}^* : \text{P} = 1.85$; $\text{S} = 1.70$; $\text{Si} = 2.0$
it follows that $r_T^* : \quad 1.59; \quad 1.47; \quad 1.85$.

Thus, on the basis of approximations a), b) and c), the r_T^* values accepted for the design of the calottes are

1.60 for phosphorus
1.47 for sulphur, and
1.85 for silicium.

It should be noted, however, that even the most doubtful estimate, i.e. that for Si, does not seem to be outside reality, to say nothing of the fact that no support for the $(r_{\min}^*)_{\text{Si}} = 2.0$ value suggested by BRIEGLER has been found in the literature.

In the case of carbon atoms, covalently bound by a pair of π -electrons, further in the case of the corresponding $\sigma\pi$, or $\sigma\pi\pi$, or $\sigma p\pi$ bonds of oxygen and of nitrogen, the van der Waals radii increase in the plane normal to the bond. The only datum for this increase is the 3.7 Å distance between layers of crystalline graphite ($r_{\min}^* = 1.85$ Å). Extrapolation of this dimension for other carbon compounds, and still more for oxygen or nitrogen compounds, seemed to promise rather doubtful results, therefore indication of this is omitted in connexion with the *Eugon* calottes.

Anyhow, we might as well mention at this juncture that unfortunately no critical survey of the van der Waals values assignable to atoms in bonding has been attempted in the last 15 to 20 years. The critical reconsideration of values calculated from gas-kinetical and crystal lattice constants might be a worthwhile study.

3. Bond radii and bond sections

In a *Eugon* set eleven different atoms are represented in thirty-three types of bonding. The distances between centres of each in different types of bonding are spectroscopy data. From these distances the so-called *bond radii* $R < r_{\ddagger}^*$ can be calculated according to the method proposed by MAGAT [1]. Hence, bond radii are distances measured (visualized) as away from the centre of an atomic nucleus as far as the electron orbitals of two atoms covalently bound interpenetrate (cf. STUART [6], p. 164, Table 42; and PAULING [4] 1960, 3rd edition, p. 225 and p. 246; further, SUTTON [19], and COTTRELL [20]).

Thus the atom calottes, designed on the basis of van der Waals radii defined in the preceding paragraph and on the basis of bond radii just mentioned, are spheres on which a plane section normal to the bond radius, the so-called *valence section* or *bond plane*, indicates covalent linkage with the similar plane of the other atom.

It is customary to distinguish between the following bond types in covalent bondings:

- a) σ -bond, e.g. paraffinic monovalency
- b) $\sigma\pi$ -bond, e.g. olefinic double bond
- c) $\sigma\pi\pi$ -bond, e.g. acetylene or nitrile triple bond
- d) $\sigma p\pi$ -bond, e.g. aromatic bond in benzene, or S=O, and N=O double bond in sulpho or nitro groups.

In order to facilitate modeling, the valence sections corresponding to each bond type are marked differently with one, two or three borings (cf. Fig. 7).

This differentiation of the valence sections serves also to prevent attempts at joining incompatible bonds together.

At the same time, these bond types indicate the variety of "bond strengths" expressed, among others, also by the length of bond radii (cf. Table VI). Further, the radii of the carbon valence sections thus formed (values a , b , c and d ; cf. Fig. 7) will also be different (cf. Table VI).

The bond planes thus formed on carbon atoms and on negative oxygen atoms were considered as normal values and it was assumed that when a covalent bond was formed with a carbon atom the other atom necessarily adjusted itself to these bond plane values. This is not only an aesthetic demand to be considered in the design of calottes but also a precondition of a true represen-

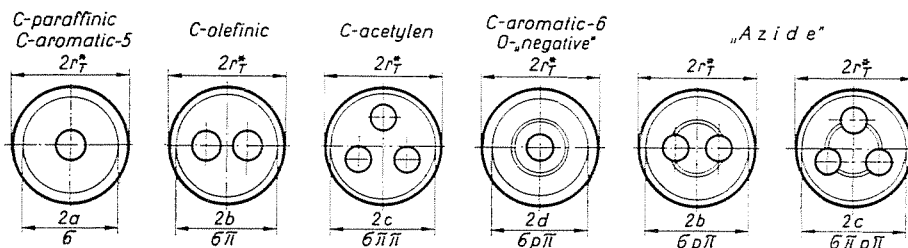


Fig. 7

tation of reality, since it is generally supposed that when a covalent bond is formed in fact the electron orbitals of the participant atoms merge smoothly, i.e. without a break or step, each into the other (coalesce). Thus it is reasonable to demand that a model should not suggest or show dimensional dissimilarity between the joined valence planes of two calottes, *viz.* according to our hypothesis the radii of the so-called normal valence sections represent the limiting boundaries, in the region of the covalent bond, of the electron orbitals of the atom involved.

Denoting the collision-radius (= electron cloud boundary) in the region of a covalent bond by r_T^0 , the condition of a smooth coalescence of the two electron clouds in the case of a joining atom X is

$$\text{for a } \sigma\text{-bond, } (r_T^0)_X = a^2 + (R_\sigma)_X^2 \quad (12a)$$

$$\text{for a } \sigma\pi\text{-bond, } (r_T^0)_X = b^2 + (R_{\sigma\pi})_X^2 \quad (12b)$$

$$\text{for a } \sigma\pi\pi\text{-bond, } (r_T^0)_X = c^2 + (R_{\sigma\pi\pi})_X^2 \quad (12c)$$

$$\text{for a } \sigma\rho\pi\text{-bond, } (r_T^0)_X = d^2 + (R_{\sigma\rho\pi})_X^2 \quad (12d)$$

Since a , b , c and d are functions of temperature, also r_T^0 is a function of temperature.

Also for the design of other atom calottes the six valence section values, as defined for the four bond types in Table VI, have been accepted. We found

that in the case of all the *oxygen* and *sulphur* calottes designed on the basis of the corresponding r_T^* and R values their radii of valence sections agree with the radii of the corresponding normal sections at an accuracy of 1 to 2 per cent, or 0.1 to 0.2 mm! Consequently the spherical surfaces of the oxygen, and of the sulphur calottes fit without a break the corresponding valence planes and thus give an adequate representation of the hypothesis that electron clouds coalesce.

In the case of the other atoms (H, N, F, Cl, Br, I, P, Si) the valence sections of calottes designed on the basis of r_T^* radii and covalent bond radii R accepted in the literature would significantly differ (by 10 to 30 per cent, i.e. 1 to 3 mm) from the radii of normal values defined before. Design and correction of these calottes are dealt with in the paragraphs that follow.

Table VI
Normal types of bonding

Calotte type	Bond type	Bond radius	Radius of the valence sections
for $(r_T^*)_C = 1.30 \text{ \AA}$			
1. Paraffin C	σ	$R_\sigma = 0.770 \text{ \AA}$	$a^2 = (r_T^*)_C^2 - (R_\sigma)_{\text{paraff}}^2 \dots (11/a);$ $a = 1.0475 \text{ cm}$
2. 5-membered unsaturated	σ_{ring}	$(R_\sigma)_{C-O} = 0.725$	$a'^2 = (r_T^*)_C^2 - (R_\sigma)_{\text{furan}}^2 \dots (11/a');$ $a' = 1.0791 \text{ cm}$
3. Olefin C	$\sigma\pi$	$R_{\sigma\pi} = 0.665$	$b^2 = (r_T^*)_C^2 - (R_{\sigma\pi})_{\text{olefine}}^2 \dots (11/b);$ $b = 1.117 \text{ cm}$
4. Acetylene C	$\sigma\pi\pi$	$R_{\sigma\pi\pi} = 0.605$	$c^2 = (r_T^*)_C^2 - (R_{\sigma\pi\pi})_{\text{acetylene}}^2 \dots (11/c);$ $c = 1.151 \text{ cm}$
5. Aromatic C	$\sigma p\pi$	$R_{\sigma p\pi} = 0.695$	$d_C^2 = (r_T^*)_C^2 - (R_{\sigma p\pi})_{\text{arom}}^2 \dots (11/d_C);$ $d_C = 1.0986 \text{ cm}$
when $(r_T^*)_{Ox} = 1.23 \text{ \AA}$			
6. Negative O	$\sigma p\pi$	$R_{\sigma p\pi} = 0.50$	$d_O^2 = (r_T^*)_{Ox}^2 - (R_{\sigma p\pi})_{\text{neg. Ox}}^2 \dots (11/d_O);$ $d_O = 1.1280 \text{ cm}$

1. According to formulae (11), the radii of valence section planes a , b , c and d , are also functions of temperature!

2. The bond radii, $R_{\sigma\pi} = 0.675$, and the radii of valence sections, $b' = 1.110$, of C=C atoms in five-membered unsaturated (furan, pyrrole, thiophene, cyclo-pentadiene) ring do not significantly differ from values found for olefins, therefore these have not been considered as separate valence sections.

3. In the preparation of the models the six normal values of the four types mentioned have been taken into account. In some special instances slight deviations are possible, so e.g. the single bond of the acetylene carbon atom $R_\sigma = 0.75$, or even in the case of conjugated double bonds $R_\sigma = 0.752$. These fine details cannot be considered, else the set is made needlessly confusing.

4. Deformation of electron clouds of bonded atoms

(Corrections of atomic radii)

41. Calottes of halogen atoms

It was BRIEGLEB [5] who first noticed that the van der Waals radius r of halogen atoms in simply bonded (non-polarized) molecules (e.g. Hal_2) is shorter than the radius r' or r^* of atoms in polar covalent bonding in organic molecules (cf. Table II). At the same time he pointed out that e.g. in the CCl_4 molecule the distance Cl—Cl was smaller ($d_i = 2r_i = 2.9 \text{ \AA}$, more accurately 2.88 \AA) than the $2r_T^*$ value 3.1 \AA found from the angular distance of two different CCl_4 molecules. On the basis of Figs 5 and 8, the value $d_i = 2r_i$ can be calculated according to the cosine theorem

$$d_i^2 = 2(R_C + R_{\text{Hal}})^2 \cdot (1 - \cos 109^\circ 28') = \frac{8}{3} (R_C + R_{\text{Hal}})^2. \quad (13)$$

From this BRIEGLEB concluded that the electron clouds of halogens deformed into a "pear-like shape" ("birnenförmig") and, according to his suggestion, this has been expressed by LEYBOLD's in their models by having the edges that emerge at the valence sections of the halogen atoms rounded off (cf. Fig. 5). BRIEGLEB utilized this discovery in the stereo-chemistry of ortho-dihalogen derivatives [5].

From the co-ordination number of compounds and from bond distance, $(2R)$ THEILACKER [18] calculated similar r_i values. Since both BRIEGLEB and THEILACKER calculated the r_i values from bond radii R , r_i values are invariant to temperature.

According to the accepted explanation of the negative polarity of covalently bound halogen atoms this is due to the electrophobic effect of the carbon atom and it is supposed that, with reference to the positive atomic nucleus, the centre of the electron cloud of the bonded halogen is shifted outward by the covalent bond.

On the basis of this picture it is possible to suggest another way for the design of the electron cloud of *negatively polarized atoms at end position* (Fig. 8 and Table VII).

Let $d_i = 2r_i$ stand for the distance between Hal atoms within the compound CHal_4 . BRIEGLEB considers this radius as the limiting boundary of the Hal electron cloud in the $\alpha = \pm 70.5^\circ$ region of the valence radius (cf. Fig. 8). Significantly, this value is in very good agreement with the r_T^0 value (Table VII) drawn to the periphery of the valence section of radius a as defined by us for the σ bond (the value r_T^0 is a function of temperature, while r_i was not).

In turn, this r_T^0 value is considered by us as the limiting value of the electron cloud of a Hal atom, in the region of a covalent bond. This r_T^0 value is

smaller than the r_T value for a non polar bond, in agreement with the fact that in the region of a covalent bond the electron cloud of a Hal atom becomes contracted. On the other hand, already BRIEGLER has shown that the original electron cloud r_T grew elongated, in the direction of the valence radius, to an r_T^* value. But *this elongation is ascertainable, from lattice constant data, exclusively in the normal direction on the covalent bond plane.*

Thus the electron cloud of a Hal atom in a negatively polarized bond is pear-like in shape that (measured from the positive atomic nucleus) grows

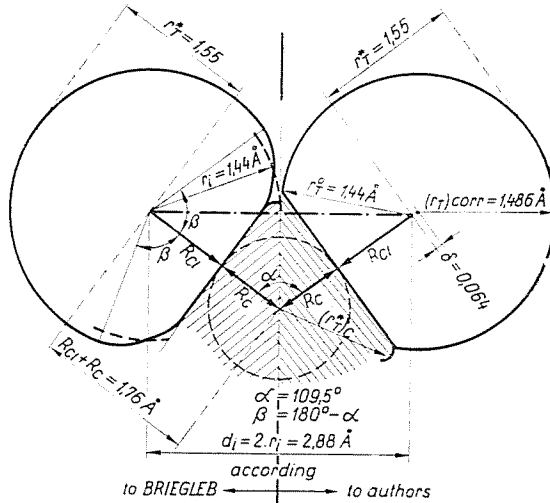


Fig. 8

from r_T^0 up to the value r_T^* . In an approximate form, this deformation of the electron cloud can be expressed so that the centre of the electron cloud is shifted in respect to the centre of the atomic nucleus by a distance δ and from this "electron centre" the electron cloud is designed with a radius $(r_T)_{\text{corr}}$ so that the bond plane of radius a defined by the paraffin carbon is arrived at.

The calculation of $(r_T)_{\text{corr}}$ becomes clear when reference is made to Fig. 8, as

$$(r_T)_{\text{corr}} + \delta = r_T^* \quad (14)$$

and
$$(r_T)_{\text{corr}}^2 = a^2 + (R + \delta)^2 = a^2 + [R + r_T^* - (r_T)_{\text{corr}}]^2$$

$$(r_T)_{\text{corr}} = \frac{a^2 + (R + r_T^*)^2}{2(R + r_T^*)} \quad (15)$$

Approximately,
$$(r_T)_{\text{corr}} \simeq \frac{r_T^0 + r_T^*}{2} \quad (16)$$

Table VII

Effective radii (Wirkungsradien) of covalently bonded polar halogen atoms (cf. Fig. 8)

	F	Cl	Br	I
1. Valence radius, R_{Hal}	0.64	0.99	1.14	1.35
2. v.d.W. radius in non-polar molecules				
a) r_T , MAGAT [1]	1.21	1.51	1.64	1.80
b) r_T , BRIEGLEB [5]	—	1.51	1.64	1.71
3. In polar bonding				
31. minimum values of the v.d.W. radius				
a) r_i , THEILACKER [18]	1.12	1.45	1.62	1.84
b) r_i , formula 13, following BRIEGLEB	1.15	1.44	1.56	1.715
c) r_T^0 , formula 12a, according to the authors	1.228	1.44	1.55	1.693
32. maximum v.d.W. radius of the atom r_T^* , BRIEGLEB [5]	1.30	1.55	1.75	1.90
33. "mean" value of v.d.W. radius				
a) $\frac{r_T^0 + r_T^*}{2}$	1.264	1.495	1.65	1.796
b) $(r_T)_{\text{corr}}$ (designed geom. cf. Fig. 8 and formula 15, resp.)	1.253	1.486	1.635	1.785
$\delta = r_T^* - (r_T)_{\text{corr}}$	0.047	0.064	0.115	0.115

N.B.

$$r_i \approx r_T^0 < r_T < r_T^*$$

and

$$(r_T)_{\text{corr}} \approx \frac{r_T^0 + r_T^*}{2}$$

42. Nitrile nitrogen ($R_{\sigma\pi\pi} = 0.547$; $r_T^* = 1.40$)

No data like those for halogens are, of course, available for nitrile nitrogen, but since here it is also an atom at end position that we deal with, the deformation of its electron cloud can be calculated on the basis of formulae 12c and 13 (using $c = 1.1510$ instead of a): $r_T^0 = 1.274$ and so: $(r_T)_{\text{corr}} = 1.311$, and $\delta = 0.089$.

43. Hydrogen ($R_\sigma = 0.30$; $r_T^* = 0.95$)

As known, hydrogen atoms in organic compounds always show positive polarity. Thus, in contrast to the halogens, in the case of covalent bonding the electron cloud is shifted towards the carbon atom. This fact emerges also when the bond planes are studied: the radius of the plane of the σ -bond cal-

culated from hydrogen data would be by 15 per cent smaller than the $a = 1.0475$ value calculated from the paraffin carbon.

In modeling, the electrophilic effect of the carbon in a C—H bond is shown by an extension of the bond plane of the hydrogen that results in a "helmet"-like form for the hydrogen calottes (cf. Fig. 9).

Note. Should we, according to the "centre shift method" suggested by STUART, apply by a positive correction of the radius a of the valence section an $(r_T)_{\text{corr}}$ value (1.064 Å) for hydrogen too, then, in certain cases, by the models a slight steric hindrance would be suggested that in fact does not exist.

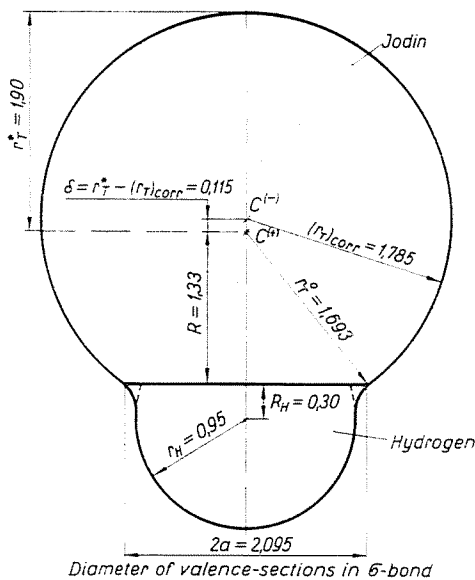


Fig. 9

44. Modelling of atoms with bond planes more than one

Finally, after the well founded corrections discussed before, only the study of the electron clouds of three kinds of bonded atoms i.e. P, N, and Si remains to be attempted.

Phosphorus ($R_\sigma = 1.10$, $R_{\sigma\pi} = 1.00$, $r_T^* = 1.60?$, $(r_T^*)_{\text{mod}} = 1.518$)

In Paragraph III. 2 we have seen that the van der Waals radius of phosphorus could only be estimated on the basis of analogies, thus it was more or less doubtful.

The valence sections (of the radii a , and b) can only be kept constant if the value of r_T^* is reduced (modified) to 1.518 Å. A similar value, 1.55 Å, is quoted by STUART [6]. Calculating with this $r_T^*_{\text{mod}}$ values $a = 1.0475$, and $d_0 = 1.128$, in good agreement, are obtained.

Nitrogen ($R = 0.70$, $r_T^* = 1.40$?, $(r_T^*)_{\text{mod}} = 1.26 - 1.311$)

If the single bond plane of the nitrogen is made equal to the normal bond plane of the paraffin carbon then $r_{T,\text{mod}}^* = 1.26$ results for the amino nitrogen and for the tetrahedric nitrogen. Also the corresponding b , and d bond plane radii designed with the collision radius 1.26 for the amide-, nitro-, and azo-nitrogen atoms agree tolerably well with the normal value of the valence sections deduced from the carbon atom (cf. Table VI).

It should be noted that the r_T^* value for the nitrogen atom is the most doubtful in the literature and especially that data for nitrogen in organic bonding are lacking. (THEILACKER calculated a singularly low $(r_i)_{\text{Nitr}} = 1.17$ Å value only from metal nitrides MeN_3 of linear structure.)

When noting all this, we did not want to deviate very far from values usually given in the literature, therefore we designed these nitrogen atoms with a radius $r_T^* = 1.311$ cm, since in this way the dimensions of the normal valence sections that form the basis of design could be approximated best (it is true, however, that this compromise resulted in a 10 per cent distortion of bond radii).

A special case is presented by the *azide nitrogen*. Here the normal values of the two 180° valence sections unequivocally demanded that $r_{T,\text{mod}}^* = 1.278$ Å.

For *nitrogen atoms in cyclic structure* (aromatic or quaternary pyridinium, pyridine, and pyrrole) van der Waals radius was taken as the original $r_T^* = 1.40$ Å value, irrespective of points of view of aesthetics, and rounding off was resorted to in order to arrive at the normal value at the bond plane.

The *pyrazole nitrogen* is a symbol only: since no measured data were available, this was designed on the basis of data for a carbon in a five membered unsaturated ring, in fact, it is such a carbon that is replaced by the nitrogen in question.

Silicium ($R_c = 1.17$, $r_T^* = 1.85$?, $(r_T^*)_{\text{mod}} = 1.57 - 1.69$)

This case is similar to that of nitrogen. If the normal value of the bond plane were maintained, $r_{T,\text{mod}}^* = 1.57$ Å! resulted. As a compromise, the calotte was designed to 1.69 cm, thereby σ -bond radii were distorted by about 13 per cent.

Collation of the van der Waals radii by BRIEGLEB, STUART and the authors cf. Fig. 18.

5. Modelling of bond angles

The bond angles of bivalent and polyvalent atoms are functions not only of the character of the bonds but also of the kinds of atom that enter the structure. Thus in the preparation of calotte models we were compelled to

adopt the mean value of the angles found in compounds. Exceptions are the five membered heterocycles where through a special device we succeeded with one calotte flexibly to demonstrate the variations of the bond angle in function of the hetero atom.

In what follows, some problems in connexion with the modelling of bond angles will be briefly discussed.

51. *The three bonds of olefinic carbon are in the same plane.* The three angles are fixed at 120° on the calotte though, especially with halogens as substituents, in fact deviations by a few degrees occur.

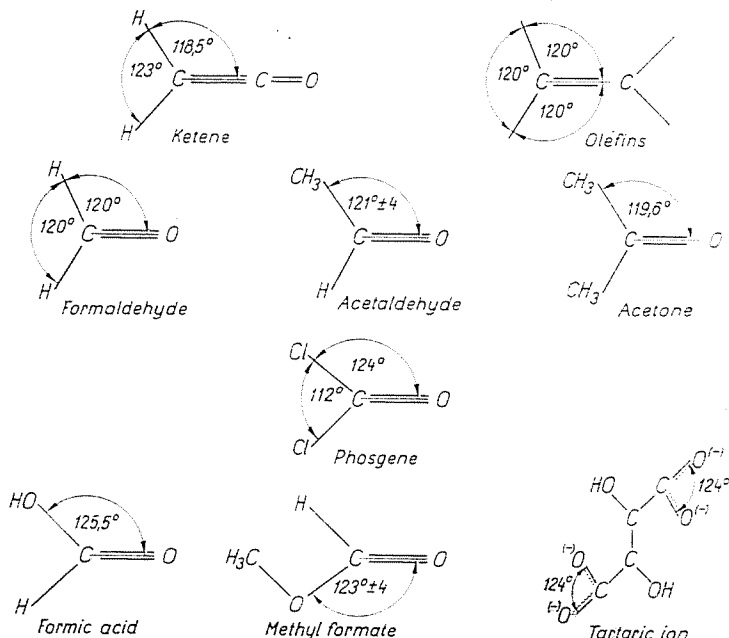


Fig. 10

52. *In the case of carbonyl carbons there is a difference according to whether an aldehyde carbonyl ($\alpha = \beta = \gamma = 120^\circ$) or a ketone carbonyl ($\alpha = 112^\circ$, $\beta = \gamma = 124^\circ$) is to be modelled.* Ketene takes an intermediary position ($\alpha = 123^\circ$, $\beta = \gamma = 118.5^\circ$). Cf. Fig. 10, and Ref. [19].

In modelling it was considered necessary to distinguish between *acid carbonyl* (= carboxyl) carbon and olefinic and carbonyl carbons: at an error of a few degrees the olefinic carbon calotte, or the aromatic carbon calotte in the case of ionic forms, lends itself for modelling the acid carbonyl, too.

53. *Ether oxygen.* In most of the compounds, the angle of the single bonds is 105° . Then, however, with $r_T^* = 1.23$ and $R_\sigma = 0.66$ values the two valence planes would intersect and thus the atoms to be linked could not be accommodate one beside the other. (In reality, obviously, it is the electron

cloud of the atoms linked that will undergo deformation.) Like other designers of calottes, we too adopted a distortion to 109° of this angle and increased R_σ values to $R_{\sigma, \text{mod}} = 0.76$ cm (cf. Fig. 11).

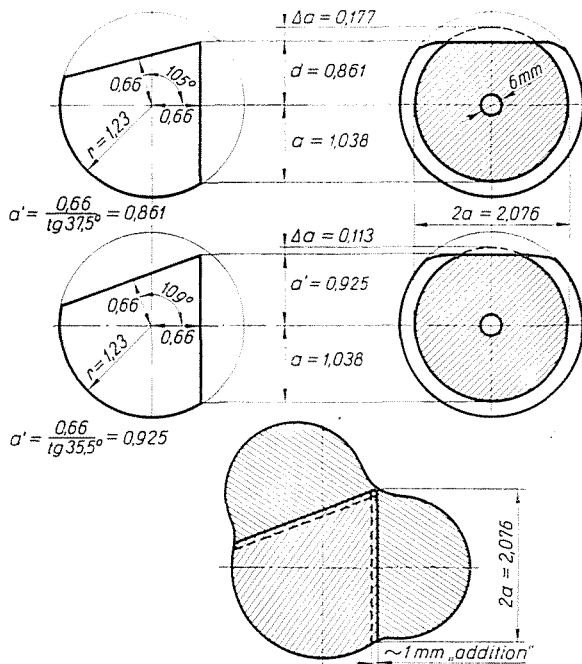


Fig. 11

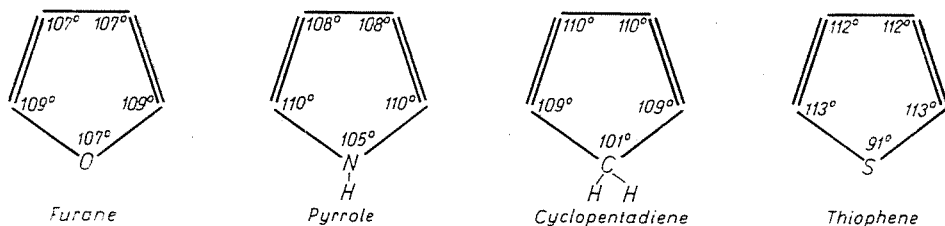


Fig. 12

54. *Five membered unsaturated ring.* Besides cyclo-pentadiene several compounds of five membered unsaturated rings with one or more hetero atoms are known. Prominent representatives are thiophene, pyrrole, and furfural. Unfortunately the bond angles of the three hetero atoms each vary within wide limits (91° , 105° and 107°), and so do bond radii ($R_\sigma = 1.04$, 0.70 , and 0.66). In consequence of this also the CCC angles of the olefinic carbon in the ring are distorted: for cyclo-pentadiene these angles are in the range 109 – 110° ,

while for the three hetero-rings mentioned they range from $112-113^\circ$, $108-110^\circ$, and $107-109^\circ$, respectively (cf. Fig. 12).

These deviations of a few degrees may add up in a ring so that ring models can be put together but with difficulty because of the stress produced. To obviate this, i.e. to allow models to be constructed stress-free, the single C—C valence planes of the olefinic carbon atoms in the five membered unsaturated ring were given a “roof-like” shape permitting a “tilting” between 112.5 and 108° on the single bond planes of these carbon calottes, and a stress-free construction of models for the compounds mentioned (cf. Fig. 13).

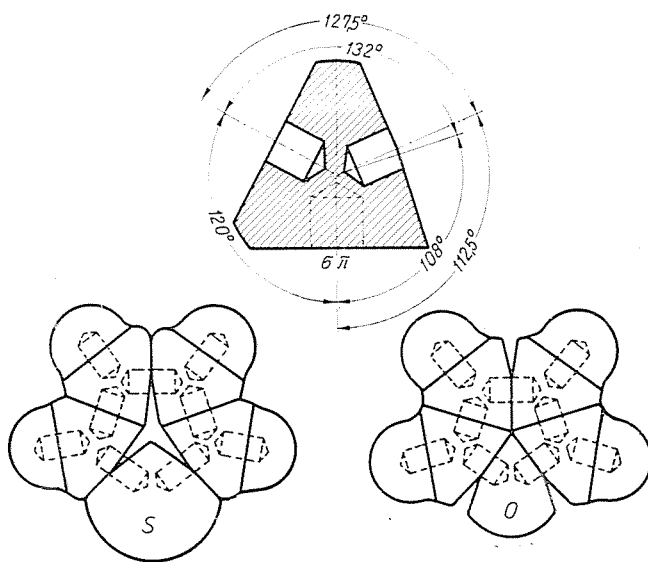


Fig. 13

This novel design of the *Eugon* calotte set permits, in case of five membered unsaturated cyclic compounds with variable bond angles, to maintain the true angles of the compounds. Therefore no stress acts in the valence bonds of molecule models.

In this instance the positive or negative stresses that in fact exist in the real compounds are symbolized by the position of the angular points between the roof-shaped tiltable valence planes (cf. Fig. 13).

N.B. The data for the “paraffin carbons” in five membered unsaturated rings slightly deviate from data pertaining to straight chain paraffins ($\alpha_{\text{CCC}} = 101^\circ$) but, at a small error, paraffinic carbon calottes may be used also in the modelling of cyclo-pentadiene with the corresponding roof-shaped cyclic olefins.

Prominent among five membered unsaturated cyclic compounds are the *azoles* (pyrazole, imidazole, the triazoles, tetrazoles, and pentazoles, further the oxo- and thio-azole, -diazole, -triazole, and -tetrazole). Common in

all these is the replacement by 1, 2, 3 or 4 so-called "pyrazole nitrogens" (azo-nitrogens) of olefinic carbons within the ring. Unfortunately, no data could be found in the literature on the bond radius and valence angles of this pyrazole nitrogen, therefore this latter was symbolized by a "five-member unsaturated carbon" calotte tinted blue. So all the azole derivatives, and even compounds with a *purine skeleton*, could be modelled!

6. The joints between calottes

These are elastic *steel cylinders*. In the case of single bonds, these allow free rotation of the two interconnected calottes around the valence axis, and still impart rigidity enough to prevent distortion (strain) of the bond angles. If greater or smaller deviations from the bond angles applied to the calottes exist in the real compound (ring stresses), then *elastic rubber joints* are used in modelling. Compounds which can only be modelled with rubber joints because

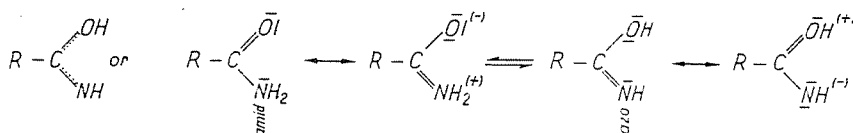


Fig. 14

of the stresses inherent in their ring, are the following: *cyclo-propane*, *cyclo-butane*, *cyclo-pentane*, *cyclo-pentadiene* and *camphor*, since the set lacks the "special aliphatic carbons in a ring" calottes. The same applies in the case of *pyranes*, *pyrones*, *flavones*, since no "oxamine-oxygen" and "pyrone-oxygen" calottes are provided.

Similarly, elastic rubber joints are used in modelling *anhydrides*, and *imides* of β -dicarboxylic acids (succinic acid anhydride and imide, phthalic acid anhydride and imide). However, it is interesting that the thio-derivatives of the same are easily modelled with the thiophene-sulphur calotte.

The tub-form of the *tropane skeleton* can be satisfactorily modelled, while the chair form (stressed) can be reconstructed only with rubber joints.

In the tropane skeleton there is such a high stress at double bond olefinic carbons that these can be joined together only with rather long rubber pieces (this symbolizes, at the same time, the highly stressed state).

N.B. On the roof-shaped bond plane of the five-member unsaturated carbon only the elastic rubber joints can be used, to provide for "tilting".

As told in the foregoing, the uniform representation in the valence planes of the various types of bonding (Fig. 7) was adopted in order to facilitate modelling. When constructing a model, care must be taken that *only plane sec-*

tions of the same valency and the same mark are joined together. This rule admits but few exceptions. These are

1. *Condensed ring systems* (anthracene, naphthalene, phenanthrene) where the "aromatic carbon" should be used for the carbon common to two

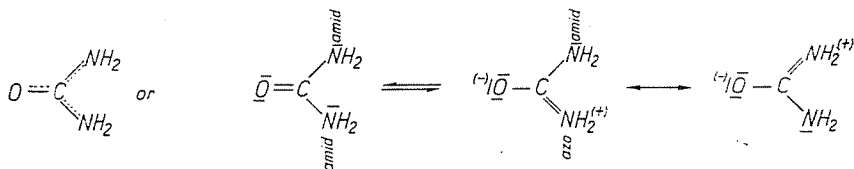


Fig. 15

rings. However, in this case the σ -valence plane of this calotte is joined up to the $\sigma p\pi$ -valence plane of the aromatic carbon of the other ring.

2. In models of *condensed systems that comprise an unsaturated C₅-ring* (benzofurane, thionaphthene, indole, purine, etc.) the two common C atoms are represented by two "five-member unsaturated carbon" calottes, i.e. by the so-called tiltable carbon, then in the six-membered ring σ and $\sigma p\pi$ planes come face to face.

3. In the case of *pyridine-N-oxide* the σ -bond of the "aromatic (quaternary) nitrogen" is joined to the $\sigma p\pi$ plane of the "negative oxygen" calotte.

4. In models of *acid amides* (lactam ring, peptide bond, mid-position nitrogen of acide hydrazide, and suphlonamide) mesomer tautomerism occurs, according to the resonance theory (Fig. 14). This is indicated by the $\sigma p\pi$ bond mark on the bond plane of the amide nitrogen linked to the carbon. Of course, in this instance σ and $\sigma p\pi$ bonds meet in the C—N bonding. If however, the acid carbonyl carbon is replaced by an "aromatic carbon" and not by an olefinic carbon, then the former faces with a $\sigma p\pi$ bond both the negative oxygen and the amide nitrogen. The same applies for the *urea* molecule (Fig. 15).

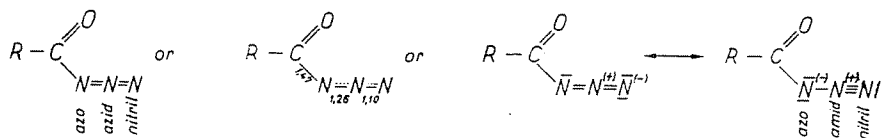


Fig. 16

5. Similarly, according to the resonance theory, *acide azides* and *diazonium salts* (*diazomethane*) can be interpreted as hydrides of polar limiting structures (cf. Figs 16 and 17). Therefore here, like in the amide-nitrogen, both valence planes of the "azide nitrogen" are marked with signs of partial bondings: $\sigma p\pi$ and $\sigma p\pi$, respectively. Consequently different bond planes are joined in modelling *viz.* in

acid azides the $\sigma\pi$ -bond of the azo-nitrogen to the $\sigma p\pi$ -bond of the azide nitrogen, and in

diazomethane the $\sigma\pi$ -bond of the olefinic carbon to the $\sigma p\pi$ -bond of the azide nitrogen, further, the $\sigma p\pi$ -bond of the azide nitrogen and the $\sigma\pi\pi$ -bond of the nitrile nitrogen come face to face in both.

Thus for azide nitrogen, like for the amide nitrogen, the joining of different bond types suggests a *mesomeric structure*.

6. *Aromatic diazonium cations* can be modelled only if one of the aromatic carbons of the benzene ring is replaced by an olefinic carbon and to this the azide nitrogen and then the nitrile nitrogen is fastened, as in the case of diazo-

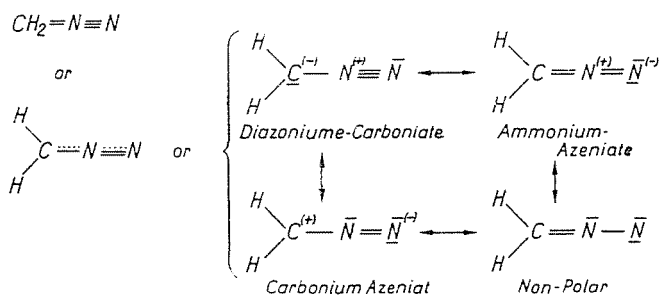


Fig. 17

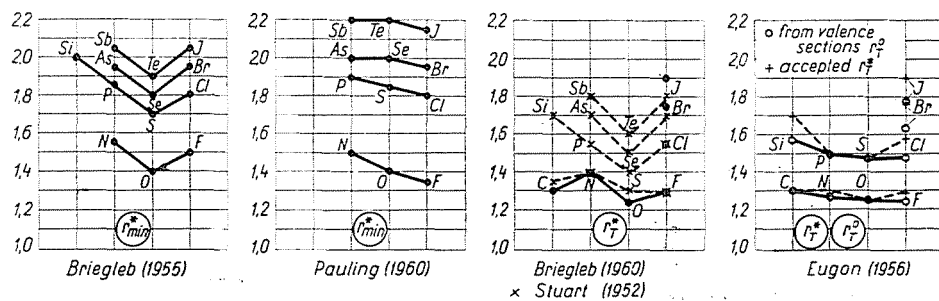


Fig. 18

methane. Thus here two irregular $\sigma-\sigma p\pi$ links occur between the carbons in the ring.

Table VIII is a list of groups of compounds that can be modelled with the Eugon set according to what has been stated in the preceding paragraphs.

7. Bond types not represented by the Eugon set

Acid carbonyl carbon can be substituted by the "olefinic carbon" or "aromatic carbon" (see § III. 52).

Carbon monoxide carbon. Fulminic acid cannot be modelled since the C=calotte is lacking. (Perhaps it can be symbolized by the allene carbon.)

Table VIII
The modelling of organic compounds

Cat No.	Model species	Assembled compounds
1.	C-tetrahedral	Paraffin Cycloparaffin-6
2.	C-olefinic	Olefin Carbonyl Double bond in carboxylic group Double bond in ring-6 Cyclotetraene Quinones Phosgene
3.	C-aromatic	Benzene Pyrene Chrysene Triphenylene Naphthalene Anthracene Tetracene Pentacene Aromatic-6 Hides
4.	C-acetylene	Acetylenes C— in nitrilic group Cyanide
5.	C-allene	Allene Ketene (thio-) cyanates (thio-) isocyanates CO ₂ COS CS ₂
6.	C-aromatic-5	Furane Thiophene Pyrrole Pyrazole Triazole Tetrazole Cyclopentadiene Indene Cumarone Indole Thionaphthene 5-ring
9.	O-single bond	Ethers Esters Lactone Alcohols O-single bond in acids Peroxide

Table VIII cont.

Cat. No.	Model species	Assembled compounds
10.	O-double bond	Aldehyde Ketone Double bond in carboxylic group Quinone Nitroso-O
101.	O-negative	Oxygen in nitro and sulfo group O-ion in anions Phenolate ionic form Amino-oxides
11.	N-amino	Amino group Amino acids Hydroxylamine Hydrazide Piperidine Terminal-N in acid hydrazides
12.	N-amide	Amide in acids Lactame-ring Intermediate-N in acid hydrazides Sulfonamide Peptide-bond e.g. in proteins
13.	N-azo	Azo-diazo-compounds Imido-ethers Guanidine Oxime-, imine-, and lactime-compounds Isocyanates Isothiocyanates
14.	N-aromatic-6 (quaterner pyridinium)	Pyridinium cation Pyridine-N-oxide
141.	N-aromatic-6 (pyridine)	Pyridine Pyridazine Pyrimidine Pyrazine Triazine Tetrazine Pentazine Quinoline Isoquinoline Acridine Phenanthrydine Naphthrydine Phenazine
15.	N-nitrile	Nitrile-compounds Cyanates, thiocyanates Terminal-N in azides Terminal-N in diazomethane N in diazonium cation

Table VIII cont.

Cat No.	Model species	Assembled compounds
16.	N-azide	Carboxylic azide Azido-compounds Intermediate-N in diazomethan and diazonium cation
17.	N-pyrrol (N-imide ring)	Pyrrol Pyrazole Imidazole Thiazole Triazole Tetrazole N-imide in purine
171.	N-pyrazole (N-azo ring)	N-azo in the same
18.	N-tetrahedral	Ammonium cations Aminoxides Ilides
23.	S-di-univalent	Mercaptans Mercaptals Dithioacids
24.	S-double bond	Thioacids, -aldehydes, -ketones Thiophosphate
25.	S-thiophene	Thiophene Thionaphthene
26.	S-tetrahedral	Sulfuric acid and esters Sulfo group Sulfoximine
27.	Phosphorus	Phosphoric acid and esters
28.	P-tetravalent	PCl ₃ Phosphines Phosphorous acid and esters

Paraffinic carbon involved in *cyclo-pentadiene* ($\alpha = 101^\circ$) can be substituted by "aliphatic carbon" ($\alpha = 109.5^\circ$) if necessary (see § III. 54).

Furane oxygen ($\alpha = 107^\circ$) can be replaced by the "ether oxygen" ($\alpha = 109^\circ$) calotte.

Pyrane oxygen (twice co-ordinated oxygen, $\alpha = 120^\circ$) may be replaced by ether oxygen, e.g. in pyrones, dioxymes, flavones, etc.

Oxonium oxygen (thrice co-ordinated $\triangleright O-$). The lack of this calotte precludes modelling of anthocyan and benzopyridinium salts, of chromylum salts, brazylium salts.

Sulphoxide sulphur (co-planar thrice co-ordinated >S=). Lack of this precludes modelling of sulphoxides.

Chelate compounds and *hydrogen bonds* cannot be represented by the *Eugon* set available at present. On the one hand, the calottes of the central metal atoms are lacking for this, on the other hand, no means has yet been provided on the oxygen or hydrogen calottes for their mechanical linking.

(To be continued)

References

- 1—18. See Part I. Periodica Polytechnica, Series CH. 12, 43 (1968).
19. SUTTON, L. E.: Tables of interatomic distances and configuration in molecules and ions. London 1958
20. COTTRELL, T. L.: The Strengths of Chemical Bonds. London 1954.

Prof. Dr. Károly TETTAMANTI } Budapest XI., Műegyetem rkp. 3.
Jenő TÖRÖK } Hungary