

SPATIAL MODELS OF MOLECULES IN CHEMICAL RESEARCH AND TUITION, III

By

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IV. Physico-chemical characteristics determinable by modelling

A molecule model is likely to deliver two kinds of information:

1. geometry, form, shape, and dimensions,
2. intramolecular motion, deformation, and energy relations of molecules.

1. *Study of the geometry of molecules*

The primary and most conspicuous advantage of a realized model is the possibility of spatial observation. Any "structural formula" drawn in whatever way on the plane of a paper will never mirror actual geometrical relations, whereas a molecular model is a "formula in three dimensions" of the given compound. It is not only in the inculcation of space-conscious chemical reasoning that models have proved to be most helpful, but they have considerably simplified the solution of a number of stereochemical problems (symmetry relations, isomerism, structural evidence) which would have been impossible else than by rather roundabout methods. Perhaps an example or two will not be inappropriate.

1.1. *Symmetry within compounds*

The so-called "caged ring systems", i.e. condensed systems made up from four rings of the chair-type conformation, are represented in the literature by various plane figures (cf. Fig. 19). However, it is rather difficult to realize from these that the units that maintain linking in three directions (symbols $-\bigcirc\langle$) are in effect apices of a tetrahedron, and that the other constituents (symbols $-\bullet\langle$) are sited on its edges. Thus the shape of the molecule approaches a regular but rough sphere which shows, at the same time, also tetrahedral symmetry.

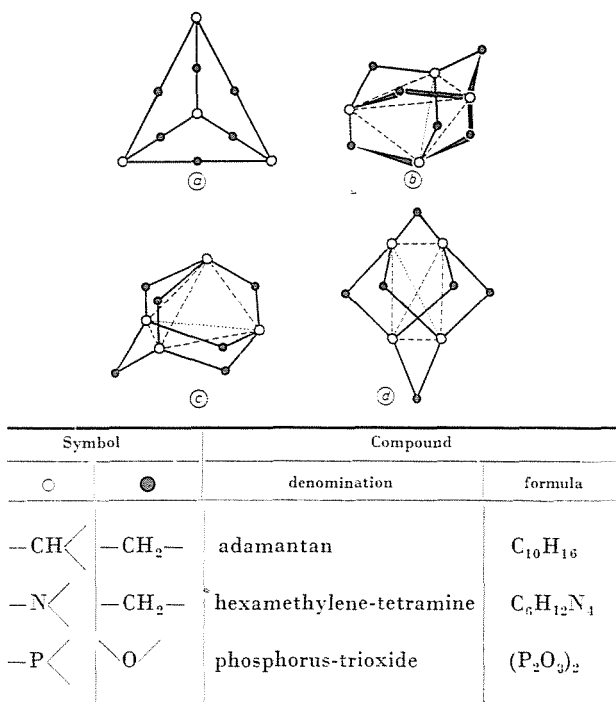


Fig. 19

1.2. Modelling of structural isomers

Among the innumerable cases, some instances well demonstrable by modelling may suffice as examples.

a) The isomerism of maleic and fumaric acids is a classic instance of

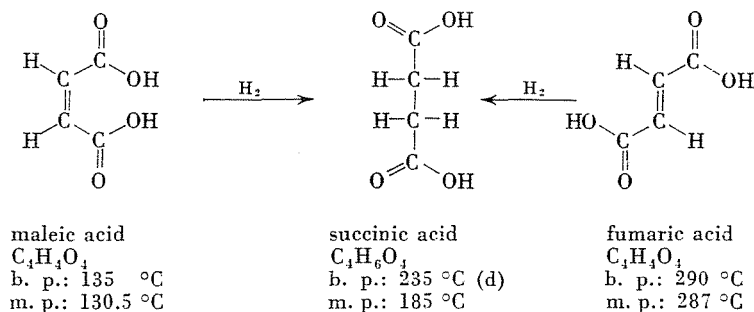
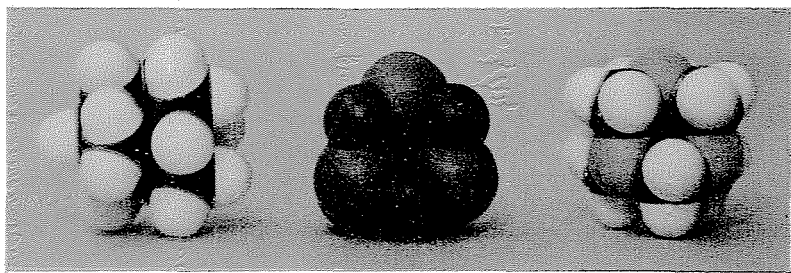
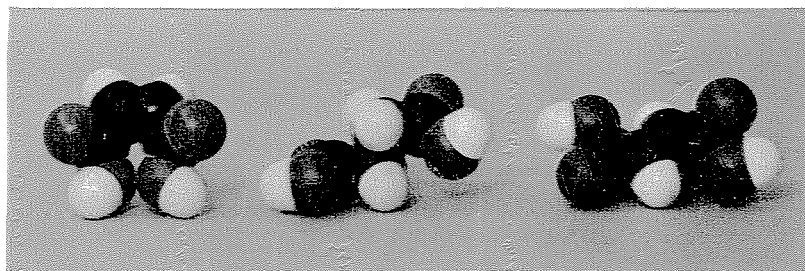


Fig. 20

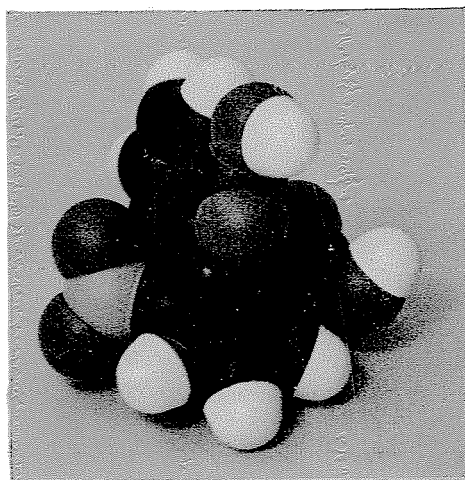
cis-trans isomerism. The two acids, with the same empirical formula, are both converted into succinic acid by addition of H₂. Maleic acid at 140 °C yields maleic anhydride, fumaric acid does not lose water under these conditions. A more intensive treatment will dehydrate fumaric acid too, resulting again in maleic anhydride. This is obvious since the spatial proximity of the two



Model 1



Model 2



Model 3

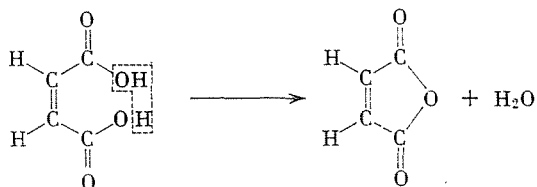


Fig. 21

carboxyl groups in maleic acid facilitates the elimination of water, whereas in fumaric acid no cyclic anhydride can be formed because of the distance in space that separates the two carboxyls. At the cost of a higher input of energy, the olefinic bond can be rotated into the maleinic structure which will then yield the anhydride. These spatial features are rather well revealed by the models, as can be explained on hand of the tetrahedral structure of the carbon atom discovered by van't Hoff a long time ago. The viewing of the model fully substantiates the original concept of VAN'T HOFF.

b) A calotte-model for 6,6'-dinitro-diphenic acid (m.p. 263 °C) is a clear piece of evidence for the fact that, due to the rather voluminous substituents, the two phenyl rings cannot freely rotate in respect of each other, hence this molecule cannot assume a co-planar structure. Owing to intramolecular hindrance this compound is an asymmetric structure and thus may be expected to show optical activity. Indeed, 6,6'-dinitro-diphenic acid can be resolved into two optically active enantio-stereomers ("atropisomerism").

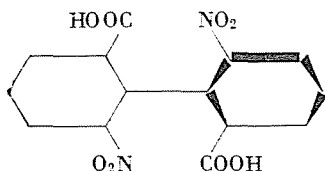
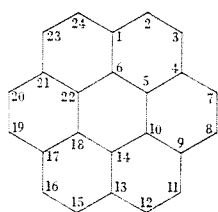


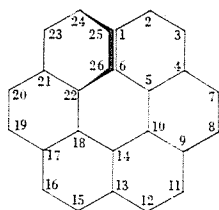
Fig. 22

However, this atropisomerism clearly demonstrated by the calotte model is not absolute, only "conditional", since with proper skill and care the two phenyl groups can in fact be turned, the nitro and carboxyl groups can be made to slide past each other exposing the rings to a slight stress. This may serve as an explanation of the experimental fact that when the proper amount of energy is imparted the atropisomers mentioned can be interconverted, i.e. racemized.

c) Also the atropisomerism of a hexa-helixan similar to coronene can be demonstrated by modelling. According to the spatial position of carbon atoms 1, 6, and 25 and 26, respectively, one isomer with a twist to the right and one with a twist to the left are possible. In conformity with the asymmetric struc-

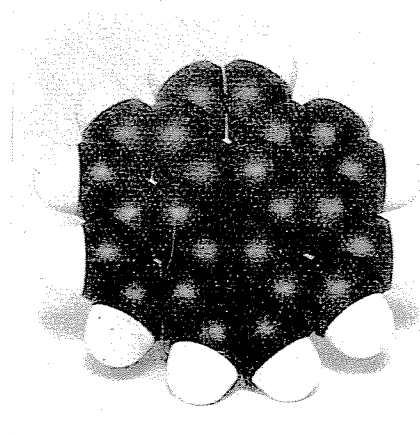


[Coronene]
 $C_{24}H_{12}$

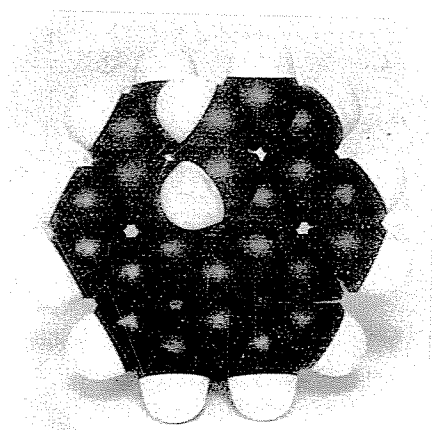


[Hexa-helixan antipodes]
 $C_{26}H_{16}$

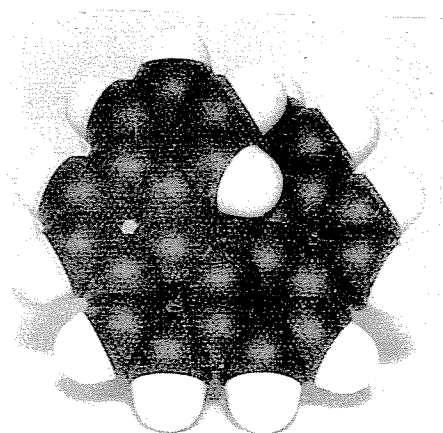
Fig. 23



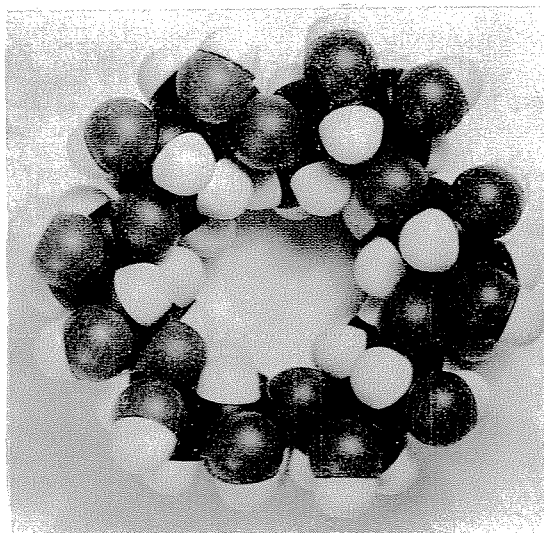
Model 4



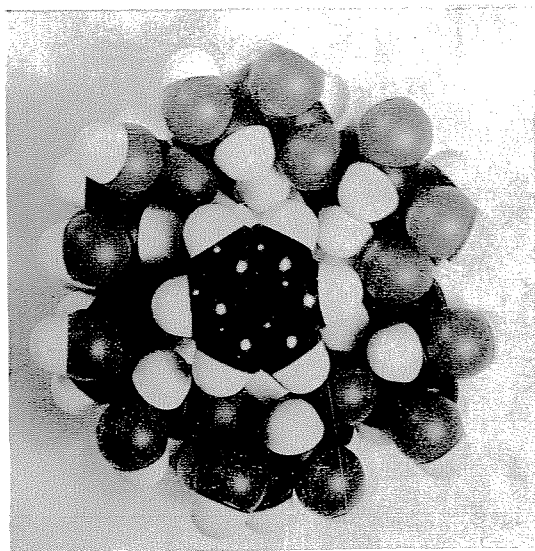
Model 5



Model 6



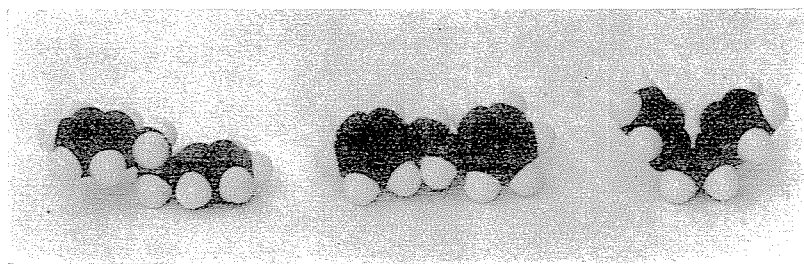
Model 8



Model 9

ture, the optically active antipodes of this compound can in fact be prepared. (Also these two optical isomers can be racemized, but, in contrast to the case of 6,6'-dinitro-diphenic acid, the attempts of the authors at this inversion on the calotte model failed: Nature is likely to be more skilful than us. Maybe the Reader will succeed!)

d) Due to the tetrahedral structure of the bridge that joins the two benzene rings of dibenzyl, this compound cannot be co-planar (cf. Fig. 24). But one



Model 7

would expect that, in view of their olefinic bridging unit, the two dehydrogenated derivatives of this compound, i.e. *cis*- and *trans*-stilbene, of the same

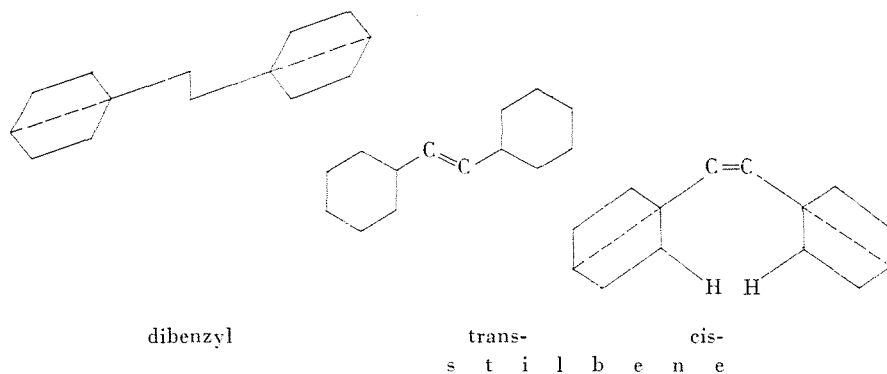


Fig. 24

empirical formula, will be co-planar molecules. Yet the calotte models clearly demonstrate that while the *trans*-derivative is indeed a co-planar structure, *cis*-stilbene can exist only in a considerably twisted form because of the strong interference of the hydrogens in *ortho* position. The same twisted shape is found by X-ray diffraction to exist in *cis*-azobenzene that contains the $-\text{N}=\text{N}-$ bridge.

1.3. *Pre-modelling, and proving the structures by models*

The search for a correct molecular structure or configuration of a compound of which a synthesis is known, or to be attempted, and proving such a structure, both on hand of molecular models, has already become current practice in organic chemical work. Proof by models is a very illustrative and simple method and therefore widely considered acceptable, as testified by a great number of publications.

To give but one example for structural evidence we may mention that the configuration of sesamines and pinoresinols, precisely the position of the carbon atoms that form the 8—8'-bridge in them, has been decisively established by FREUDENBERG et al. [21] with the help of a model built, incidentally, out of the pieces of a EUGON set.

Besides the subsequent proving by a model of the structure of compounds known and prepared, we wish to stress the importance in synthetic work of the possibilities that reside in pre-modelling or molecular designing of a compound. From the design principles discussed in the preceding communication, it appeared that the technical make-up of the calotte models did not make the construction but of atomic bondings actually possible or, the other way round, no modelling was feasible that would lead to bondings outside the realm of facts. In consequence, modelling prior to synthesis or other processing may prevent much fruitless experimental effort.

1.4. *Study of the dimensional proportions of molecules*

The accurate knowledge of the true molecular dimensions of organic compounds is today a justifiable and necessary requirement in many fields of research. This knowledge should include

a) linear dimensions of molecules, as diameters, collision distances of centres, etc., and

b) real volumes of molecules, or the space effectively filled up by them.

ad a) *Linear dimensions of molecules.* The true spatial dimensions of an organic compound existing at room temperature can be measured, with a ruler or with a slide gauge, on the model constructed. This is specially important in calculating transport coefficients where an accurate knowledge of distances of collision centres of molecules is a prerequisite of a correct calculation.

Diffusiveness of gases (Maxwell)

$$D = \frac{b \cdot T^{\frac{3}{2}}}{d_{AB}^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (17)$$

Viscosity of gases (Maxwell, Chapman, Enskog)

$$\mu = 0.499 \frac{2\sqrt{m \cdot k \cdot T}}{\pi^{\frac{3}{2}} \cdot d^2} \quad (18)$$

Heat conduction

$$\lambda = \frac{\sqrt{\frac{k \cdot T}{m}}}{\pi^{\frac{3}{2}} \cdot d^2} \cdot c_v \quad (19)$$

where d = distance of molecular centres at collision

T = temperature, °K

M = molecular weight

m = mass of one molecule

k = Boltzmann's constant

c_v = specific heat at constant volume

The determination of the average molecular diameter d by some other means, particularly for organic compounds of a more complicated structure, is beset with difficulties. The most reliable data up to now have been arrived at just by calculations based upon these gas kinetical values measured.

The measuring of the diameter of however complicated a molecule by such a simple method as modelling is of great importance especially when this molecule can assume a wide range of linear dimensions through intramolecular motion as rotation, vibration (stretched or contracted forms or states). For instance, in its coplanar form, dibenzyl mentioned before fills a space of 13 by 6 Å, measured on its calotte model, while in its contracted form it needs 7 by 7 Å. Obviously the distance between molecular centres at collision is some statistical average between these limits. The average diameter can be calculated also from the total volume of the molecule; for this the volumes of atoms in covalent bonding must be known:

$$\Sigma v_{\text{atom}} = v_{\text{molecule}} = \frac{d^3 \pi}{6} \quad (\text{Å}^3 \text{ or } \text{cm}^3) \quad (20)$$

and thus

$$d_{\text{molecule}} = \left(\frac{6}{\pi} \right)^{\frac{1}{3}} (\Sigma v_{\text{atom}})^{\frac{1}{3}} = 1.241 (\Sigma v_{\text{atom}})^{\frac{1}{3}} \quad (21)$$

ad b) Calculation of the volume of atoms and of molecules. The atomic volumina of elements can be calculated when van der Waals radii (r_T^*), and covalent bond lengths, discussed in detail in preceding paragraphs and reflecting the fundamental principles of design, are known.

Calotte volumina of carbon, oxygen, and sulphur have been calculated from r_T^* and R_σ values given in the literature (cf. our preceding paper). The volume of hydrogen was calculated according to principles of design discussed in Section III/4.3, for its so-called "helmet form" calotte. Volumina for halogens have been calculated on the basis of what is said in Chapter III, with a calotte radius $(r_T)_{\text{corr}}$ that accounts for the polarization of the electron cloud, and with the bond length R_σ taken from the literature, validating the principle that in a polar bond the electron cloud of a halogen atom is distorted. In the respective cases of the calottes for nitrogen, phosphorus, and silicon, because of the inner symmetry of the distortion of electron clouds we have calculated atomic volumina with the $(r_T^*)_{\text{mod}}$ van der Waals radii (cf. III/4.4).

Thus the atomic volumina of elements modelled as being involved only in R_σ covalent bondings (containing only single bonds) at room temperature are the following.

For the calculation of the volume of atoms in $\sigma\pi$, $\sigma\pi\pi$, and $\sigma p\pi$ bonds no reliable data are available (cf. loc. cit., 12, 51 (1968)). The only basis is the distance 3.7 Å, between the planes in graphite, which is considered in literature as the diameter of carbon atoms elongated in a direction normal to the unsaturated bond. Thus a carbon atom in an unsaturated bond may be visualized as a rotation ellipsoid of which the minor axis is 1.30 Å, in accordance with the r_T value and of which the major axis is half the interplane distance,

Table IX

Volumina of atoms in covalent bonds in polar molecules

Catalogue number		r_T^* (Å)	R (Å)	V_{atom} (Å ³)
1	C	1.30	0.77	5.24
9	O (ether)	1.23	0.66	5.67
23	S (thioether)	1.47	1.04	11.76
25	S (thiophene)	1.47	1.02	11.63
7	H	0.95	0.30	2.78*
19	F	1.253	0.607	7.17
20	Cl	1.486	1.054	12.64
21	Br	1.635	1.255	17.69
22	I	1.785	1.445	23.22
11	N ³⁺	1.26	0.70	5.21
18	N ⁴⁺	1.26	0.70	4.15
28	P ³⁺	1.519	1.10	12.30
29	Si	1.57	1.17	13.32

* Helmet form

i.e. 1.85 Å (cf. Fig. 25). It must be mentioned, however, that in the literature mainly 1.6 to 1.7 Å is the value accepted for the major axis. This small difference does not affect atomic volumina very much; for aromatic and olefinic bonds the volumina become about 0.5 to 1.5 per cent less, for acetylene and for allene carbons this decrease is about 4 per cent.

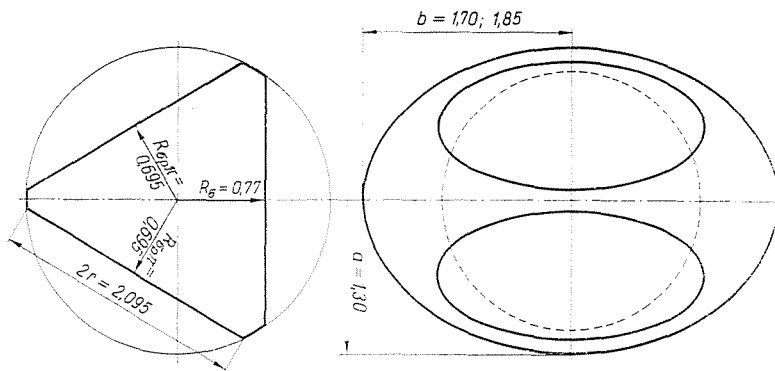


Fig. 25

Assuming conditionally the acceptability of this hypothesis, probable atomic volumina for unsaturated carbon atoms can be worked out.

By a simple additioning, according to empirical formulae, of the atomic volumes listed in Tables IX and X, the net molecular volume, at room temperature, of a given compound results and multiplying it by the Avogadro number results in the molar volume V_{mole} .

$$V_{\text{mole}} = 6.03 \cdot 10^{23} \cdot v_{\text{molecule}} = 6.03 \cdot 10^{23} (\sum v_{\text{atom}}) [\text{cm}^3/\text{mole}]$$

Note. Since, in the design of atom calottes, r_T^* , i.e. the van der Waals radii of atoms in polar bonds were used throughout, also the volumina v_{atom} given above are volumina of apolar bonds e.g. for H_2 , O_2 , etc. It is interesting to note, however, that for the non-polar Cl_2 molecule very good agreement is reached (cf. Table XI).

Table X
Approximate atomic volumina of carbon atoms in unsaturated bonds

	R_σ	$R_{\sigma\pi}$	$R_{\sigma\pi\pi}$	$R_{\sigma p\pi}$	Atomic volume (v_{atom})	
	Ångströms				$a = 1.30 \text{ Å}$ $b = 1.70 \text{ Å}$ Å ³	$a = 1.30 \text{ Å}$ $b = 1.85 \text{ Å}$ Å ³
Olefinic	0.77	0.665	—	—	6.30	6.39
Aromatic	—	—	—	0.695	6.03	6.06
Acetylene	0.75	—	0.605	—	7.44	7.74
Allene	—	0.665	—	—	7.32	7.63
Five-membered unsaturated	{ 0.77 0.725	0.675	—	—	6.08	6.12

Four times this net volume V_{mole} thus calculated gives the constant b of the van der Waals equation of state

$$b = 4V_{\text{mole}} = 4 \cdot 6.03 \cdot 10^{23} \Sigma v_{\text{atom}} \quad (23)$$

for the calculation of which several methods are described in the literature.

1. From critical constants

$$b = 4V_{\text{mole}} = \frac{RT_c}{8p_c} \quad (24)$$

2. From density values (Cailletet–Mathias extrapolation method).

3. From molecular volumes calculated on the basis of distances d of centres at collision calculated from experimental data of transport phenomena.

In lack of the possibility of, or data for, the calculations mentioned, molecular volume can be calculated according to Eq. (20), also from a molecular model built of rigid models and therefrom, according to Eq. (23), the van der Waals constant b can be calculated in turn (cf. Table XI).

It is to be seen that, compared with constants b given in the literature as calculated from critical constants according to Eq. (24), the constants b calculated on the basis of volumina of models are the same at a scatter of ± 10 per cent.

The molar volumes $(V_{\text{mole}})_{\text{calc}}$ calculated according to Eqs (20) and (22) are the real volumina of molecules. Molecular space filling must be distinguished from this, for $(V_{\text{mole}})_{\text{meas}}$ includes volumina of intermolecular gaps. Thus the so-called space filling is

$$\eta = \frac{(V_{\text{mole}})_{\text{calc}}}{(V_{\text{mole}})_{\text{meas}}}$$

and the gap volume is

$$\varepsilon = 1 - \eta \text{ (cf. Table XII).}$$

It is of interest to note that according to TITANI [23] the space filling of liquids at normal boiling point is $\eta = 0.314$. The space requirements, however, of molecules in their various states, or better their space filling ratios, require separate study.

Table XI
Net volumes of molecules

Compound	Empirical formula	M	Net volume		Constant <i>b</i> according to		°C
			<i>v</i> _{molecule}	<i>V</i> _{mole}	models	HODGMAN [22]	
			$\frac{\text{\AA}^3}{\text{molecule}}$	$\frac{\text{cm}^3}{\text{mole}}$			
1	2	3	4	5	6	7	8
Methane	CH ₄	16.03	16.34	9.48	0.03937	0.04278	92.0
Ethane	C ₂ H ₆	30.05	27.13	16.34	0.06536	0.06380	102.4
Propane	C ₃ H ₈	44.07	37.92	22.84	0.09136	0.08445	108.1
Butane	C ₄ H ₁₀	58.09	48.71	29.34	0.11736	0.1226	95.7
Pentane	C ₅ H ₁₂	72.11	59.50	35.84	0.1434	0.1460	98.2
Hexane	C ₆ H ₁₄	86.13	70.29	42.34	0.1693	0.1735	97.5
Heptane	C ₇ H ₁₆	100.16	81.08	48.84	0.1953	0.2654	73.6
Octane	C ₈ H ₁₈	114.19	91.87	55.33	0.2213	0.2368	93.4
Nonane	C ₉ H ₂₀	128.22	102.66	61.83	0.2473		?
Decane	C ₁₀ H ₂₂	142.25	113.45	68.33	0.2733	0.2905	94.0
Chloride	Cl ₂	70.91	25.29	15.23	0.06092	0.05622	108.3
Hydrogen chloride	HCl	36.46	15.42	9.29	0.03715	0.04081	91.0
Hydrogen bromide	HBr	80.92	20.46	12.32	0.04930	0.4431	111.2
Water	H ₂ O	18.02	11.22	6.76	0.02704	0.03049	88.6
Hydrogen sulphide	H ₂ S	34.08	17.32	10.43	0.04172	0.04287	97.3
Hydrogen phosphide	H ₃ P	34.05	20.63	12.42	0.04969	0.05156	96.3
Dimethyl ether ..	C ₂ H ₆ O	46.05	32.80	19.76	0.0790	0.07246	109.0
Cyclohexane	C ₆ H ₁₂	84.10	64.74	38.99	0.1559	0.1424	109.4
Chloroform	CHCl ₃	119.38	45.95	27.67	0.1107	0.1022	108.3
Carbon tetrachloride	CCl ₄	149.82	55.81	33.62	0.1345	0.1383	97.2
Ammonia	NH ₃	17.03	13.54	8.15	0.03261	0.03707	87.9
Trimethylamine ..	N(CH ₃) ₃	59.08	45.90	27.65	0.1106	0.1084	102.2
Silicon hydride ...	SiH ₄	33.12	24.43	14.71	0.0588	0.05786	101
Silicon tetrafluoride	SiF ₄	104.09	42.00	25.30	0.1012	0.05571	181 !?
Acetylene	C ₂ H ₂	26.016	20.42	12.30	0.04920	0.05136	95.7
Amylene	C ₅ H ₁₀	70.08	49.77	29.98	0.11991	0.1207 n 0.1405 iso	99.34
Ethylamine	C ₂ H ₇ N	45.064	34.72	20.91	0.08363	0.08409	99.4
Diethylamine	C ₄ H ₁₁ N	73.096	56.69	34.15	0.1366	0.1392	98.1
Methylamine	CH ₅ N	31.048	24.33	14.65	0.05860	0.05992	97.0
Dimethylamine ...	C ₂ H ₇ N	45.064	34.72	20.91	0.08363	0.08570	97.5

Table XI continued

Compound	Empirical formula	M	Net volume		Constant <i>b</i> according to		$\frac{b}{M}$
			<i>v</i> _{volume}	<i>V</i> _{mole}			
			$\frac{\text{\AA}^3}{\text{molecule}}$	$\frac{\text{cm}^3}{\text{mole}}$	models	HODGMAN [22]	
1	2	3	4	5	6	7	8
Propylamine	C ₃ H ₉ N	59.080	45.90	27.65	0.1106	0.1090	101.4
Dipropylamine . . .	C ₆ H ₁₅ N	101.19	67.80	40.84	0.1633	0.1820	89.7
Ethyl chloride . . .	C ₂ H ₅ Cl	64.496	37.00	22.85	0.09140	0.08651	105.6
Ethyl sulphide . .	C ₄ H ₁₀ S	90.18	60.48	36.42	0.1457	0.1214	120.0
Ethylene chloride	C ₂ H ₄ Cl ₂	98.944	48.99	29.51	0.1180	0.1086	108.0
Ethylene bromide	C ₂ H ₄ Br ₂	187.846	59.07	35.58	0.1423	0.08664	164.2
Toluene	C ₆ H ₅ C	92.064	63.62	38.32	0.1533	0.1463	104.7
Benzene	C ₆ H ₆	78.008	52.83	31.82	0.1273	0.1154	110.3
Aniline	C ₆ H ₇ N	93.064	60.82	36.63	0.1465	0.1369	107.0
Bromo-benzene . . .	C ₆ H ₅ Br	156.956	67.74	40.80	0.1632	0.1539	106.0
Chloro-benzene	C ₆ H ₅ Cl	112.496	62.70	37.76	0.1511	0.1453	103.9
Iodo-benzene	C ₆ H ₅ I	203.950	73.27	44.13	0.1765	0.1656	106.5
Fluoro-benzene . . .	C ₆ H ₅ F	96.04	57.23	34.47	0.1379	0.1286	107.2
m-Cresol	C ₆ H ₅ CO	108.064	69.29	41.74	0.1669	0.1607	103.8
m-Xylene	C ₆ H ₁₀ C ₂	106.08	73.41	44.22	0.1769	0.1772	99.8
Xylidine	C ₆ H ₁₁						
	C ₂ N	121.18	77.16	46.47	0.1859	0.1970	94.3
Diphenyl	C ₁₂ H ₁₀	154.08	100.11	60.30	0.2412	0.2480	97.2
Naphthalene	C ₁₀ H ₈	128.16	82.48	49.74	0.199	0.1937	97.3
Phenetole (ethyl phenyl ether) . .	C ₆ H ₁₀						
	C ₂ O	122.08	80.08	48.23	0.1929	0.1963	98.2
Ethyl-benzene	C ₆ H ₁₀ C ₂	106.08	74.41	44.82	0.1793	0.1667	107.5
Propyl-benzene . . .	C ₆ H ₁₂ C ₃	120.096	85.20	51.32	0.2053	0.2028	101.2

2. Study of the possibility of reactions of molecules, and of their intramolecular conformations

2.1. Possibilities of reaction

A necessary condition for a compound to be reactive is that the functional groups of its molecules be accessible to the reagent partner. This accessibility is mirrored correctly and true to scale by the models.

To allow correct deductions concerning spatial accessibility or hindrance, the design of the models has provided also some technical aids. The electron pair π that participates in bonding always forms a rigid connexion between

Table XII

Space filling of organic compounds in the liquid state at boiling point

Compound	Empirical formula	B. p. °C	Net molar volume; model (V_{mole}) number cm ³ /mole	Molar volume measured at boiling point (V_{mole}) _{meas} = = M/ρ cm ³ /mole	Space filling η	Free space $\epsilon = 1 - \eta$
Methane	CH ₄	-161.5	9.84	37.7	0.261	0.739
Ethane	C ₂ H ₆	- 88.3	16.34	54.8	0.298	0.702
Propane	C ₃ H ₈	- 48.2	22.84	75.2	0.300	0.700
Butane	C ₄ H ₁₀	- 0.6	29.34	96.5	0.304	0.696
Pentane	C ₅ H ₁₂	36.2	35.84	118.3	0.303	0.697
Hexane	C ₆ H ₁₄	69	42.34	140.6	0.301	0.699
Heptane	C ₇ H ₁₆	98.4	48.84	164.1	0.298	0.702
Octane	C ₈ H ₁₈	125.8	55.33	187.0	0.295	0.705
Nonane	C ₉ H ₂₀	150.8	61.82	210.9	0.293	0.707
Decane	C ₁₀ H ₂₂	174	68.33	235.6	0.290	0.710
Undecane	C ₁₁ H ₂₄	195.8	74.83	261.6	0.286	0.714
Dodecane	C ₁₂ H ₂₆	214.5	81.33	287.5	0.283	0.717
Tridecane	C ₁₃ H ₂₈	234	87.83	314.1	0.280	0.720
Tetradecane	C ₁₄ H ₃₀	252.5	94.33	344	0.274	0.726
Pentadecane	C ₁₅ H ₃₂	270.5	100.82	367	0.275	0.725
Hexadecane	C ₁₆ H ₃₄	287.5	107.32	396	0.271	0.729
Heptadecane	C ₁₇ H ₃₆	303	113.82	424	0.268	0.732
Octadecane	C ₁₈ H ₃₈	317	120.32	454	0.265	0.735
Nonadecane	C ₁₉ H ₄₀	330	126.82	493.5	0.262	0.738
Eicosane	C ₂₀ H ₄₂	350	133.32	513	0.259	0.741
Methanol	CH ₄ O	64.7	13.26	42.8	0.309	0.691
Ethanol	C ₂ H ₆ O	78.5	19.76	62.1	0.318	0.682
Propanol	C ₃ H ₈ O	97.2	26.26	81.5	0.322	0.678
Butanol	C ₄ H ₁₀ O	117.7	32.76	102	0.321	0.679
Amyl alcohol	C ₅ H ₁₂ O	138.39	25	126.7	0.317	0.683
Hexanol	C ₆ H ₁₄ O	157.2	45.75	146.4	0.313	0.687
Propanol	C ₇ H ₁₆ O	176	52.25	168.7	0.309	0.691
Dimethyl ether	C ₂ H ₆ O	- 23.7	19.76	62.7	0.315	0.685
Diethyl ether	C ₄ H ₁₀ O	34.6	32.76	106.4	0.308	0.692
Dipropyl ether	C ₆ H ₁₄ O	91.0	45.75	151.3	0.302	0.698
Dibutyl ether	C ₈ H ₁₈ O	142.0	58.82	197.8	0.297	0.703

the two covalent atoms. A covalent pair of atoms joined by a pair of electrons σ can rotate around the line between the centres of the atoms involved, thus an organic molecule may possess several atoms or groups of atoms which can rotate in this way.

The known calotte models, thus also the EUGON system, allow, through their steel springs that represent the σ bond, the rotation of the parts joined together, at the same time, the joints representing double or triple ($\sigma\pi$ or $\sigma\pi\pi$) bonds are rigid also in the molecular models. The $\sigma p\pi$ or so-called partial bond is mostly involved in cyclic structures and allows motions that may actually occur without causing the disruption of the structure.

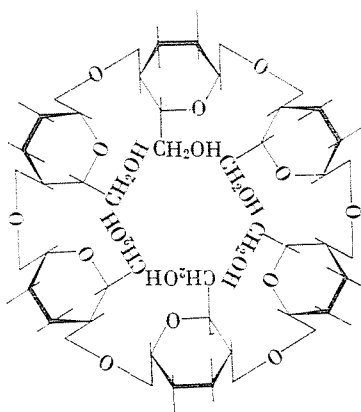


Fig. 26

Some examples, well demonstrable by molecular models, of the study of possibilities of reaction, spatial accessibility or hindrance, may be given.

Accessibility of the functional groups of ethers. The oxygen atom in the first members of the homologous series of symmetric ethers, dimethyl- and diethylether for instance, is easily accessible for any reagent also spatially. However, dipropyl ether, and ethers with still longer carbon chains can, as a result of rotations around their multiple bonds, become tangled up in such a way that the oxygen sited in the centre is covered up or shielded by the aliphatic parts. This explains the reduced reactivity of these bulkier ether molecules, and also the relatively low boiling points of such higher ethers and esters (unpublished boiling point rule due to co-authors K. T.)

α -Schardinger dextrin (cf. Fig. 26), consisting of 6 glucose molecules arranged in a cycle, is well soluble in water because of its oxygen atoms and hydroxyl groups. It is a well known fact that upon addition of some benzene to the aqueous solution of this dextrin it will crystallize out with one mole of benzene of crystallization. With benzene derivatives this will not occur. It is

easy to demonstrate the explanation. It can clearly be seen that the benzene molecule fits the middle of the dextrin ring very well and that the hydrogens of benzene can form secondary bonds with the oxygens of the dextrin. A benzene derivative, iodobenzene for instance, does not find room enough in the inner aperture of the dextrin ring, thus cannot establish secondary bonds with it and cannot affect its solubility in water.

2.2. Conformational motions, and energy states

Motions allowed within a molecule give some approximate information also about its stability, and internal energy conditions. Thus the rotation around an electron pair σ discussed in the foregoing may be hindered not only by a spatial or material barrier but also by repulsion potentials acting within the molecule. Conformational motions of saturated cyclic compounds furnish the best studied, and known, example of intramolecular variations of shape and energy levels.

Conformations, and corresponding energy levels, of cyclohexane. Two conformations, the so-called chair, and boat forms are known. The internal energy contents of these forms is not the same. Fig. 27 shows that, compared to the boat form, the chair form is of an energy level lower by about 7.5 kcal/kmole, thus this must be the more stable one. This is indeed the case; experimental data confirm that the ratio of the conformations of cyclohexane is 1 : 1000 in favour of the chair form [24]. On hand of this figure we may more closely study the respective possibilities of the various states of cyclohexane.

The only stable form of the chair type exists in two stereomers that are mirror images of each other. In contrast, the boat type structure may exist in several "sub-formations" each convertible into any other at the cost of a little energy imparted. One carbon atom, by successive turnings over 36.5° each, severally establishes new "regular" boat formations, thus by one turning round over 109.5° it passes through 4 regular boat structures (1, 4; 2, 5; 3, 6; 1, 4). However, these regular 4 boat structures are less probable states because of the resulting proximity (1.8 Å) of two of their hydrogen atoms (bowsprit—flagpole interaction, bond opposition). Due to the repulsion effect between the opposed two hydrogen atoms the molecule will seek a more stable state, one that is at an energy level lower by about 1.7 kcal/kmole. This more stable boat formation is designated as the skew boat form because, compared to the regular one, it has a somewhat distorted, twisted shape. In between the 4 regular forms 3 such irregular ones exist, each at a turn over 36.5° .

Even a symbolical representation of the spatial structures discussed is rather difficult, but their conception in space we think almost impossible without modelling. The conformations described, even the energy states marked on Fig. 27, can be demonstrated by molecular models put together from atom

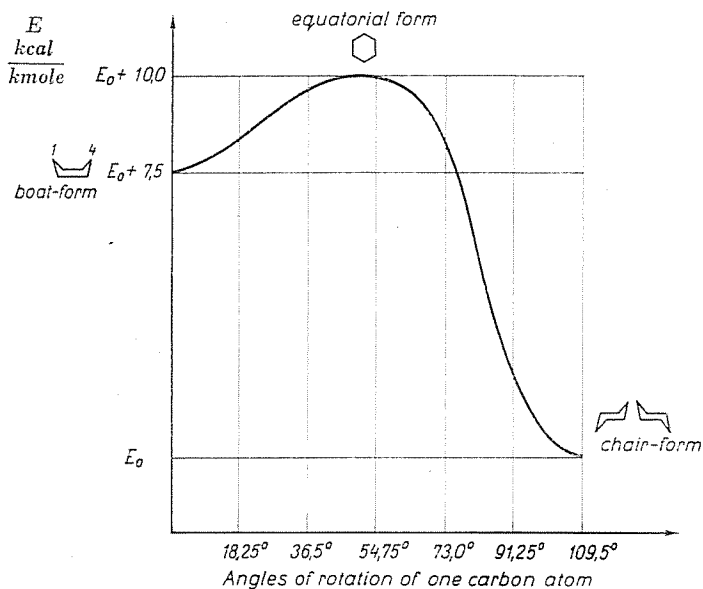
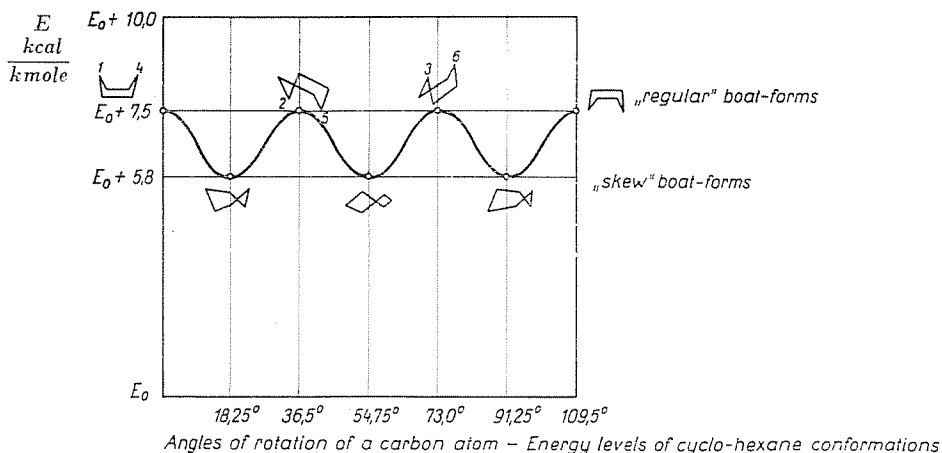
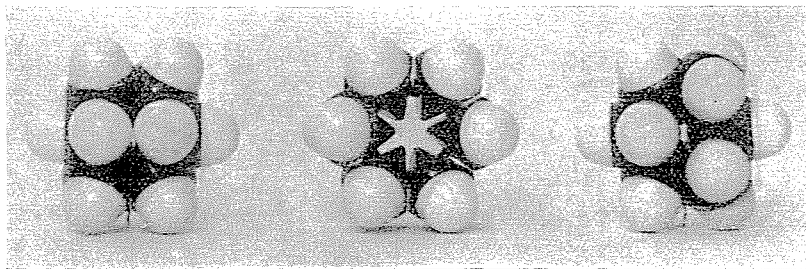
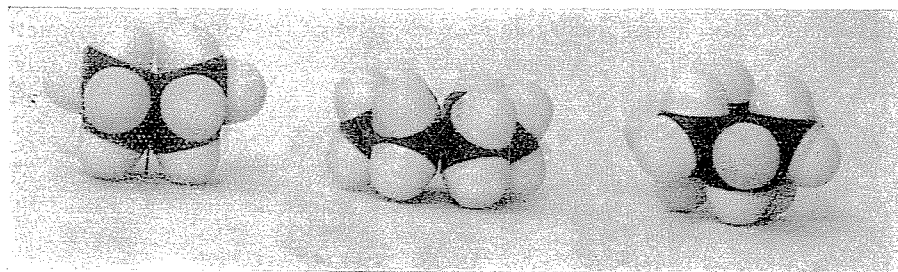


Fig. 27a. Energy levels of chair—boat conformations of cyclohexane

Fig. 27b. Energy diagram of (1.4) $\rightarrow$ (2.5) $\rightarrow$ (3.6) $\rightarrow$ (1.4) boat forms at transformation

calottes. The “regular” and the “twisted” boat forms can be easily followed on a cyclohexane model constructed of EUGON calottes. During revolving, the direction of the C—C bonds remains the same, these revolutions, on and around the elastic steel cylinders acting as “valencies”, go smoothly and stress-free solely by the relative rotation of carbon atoms (the carbon atoms of the model execute a rolling motion in respect to one another while turning as indicated

*Model 10**Model 11*

in Fig. 27). Similarly, also the interconversion of the chair and the boat structures, though different in principle from the smooth turnings mentioned, can be followed easily on a cyclohexane model built of EUGON calottes. In order to convert a regular boat structure into a chair structure, an energy barrier of about 2.5 kcal/kmole must be overcome, according to measurements. This energy is consumed when the most unlikely, the so-called equatorial configuration is formed (cf. Fig. 27). After the potential barrier has been overcome, conversion proceeds spontaneously.

When the process of a complete turn is followed on a model, the energy differences involved at the transition from one energy level to the next can be felt by the hand that manipulates the model. Beginning with the normal boat form and turning it uniformly and with care so that bonds should not be broken, the stresses affecting the steel cylinders acting as C—C bonds make themselves felt as a resistance and thus indicate the potential barrier of 2.5 kcal/kmole mentioned. As soon as this resistance is overcome the model jumps like a released spring into its most stable, i.e. chair form.

The phenomenon of twisted rings has been detected by X-ray diffraction in other cases than that of cyclohexane too. Thus, e.g. it has been found that there exists a "twisted" isomer of adamantane that contains four rings of the chair formation, and is called twistane.

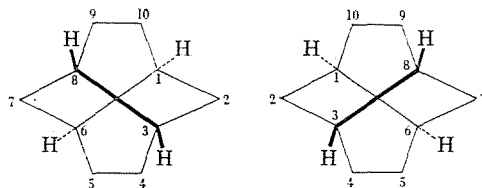


Fig. 28

These examples, picked out nearly at random from our research and lecture topics, serve but for pointing out how manyfold applications the modelling of molecules may have. It is for those well qualified further to develop this science of chemical modelling, for, apart of the excellent introductory work of FIESER [25], no literature is available to help the beginner along.

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Summary

Following a brief historical survey of how notions of the spatial modelling of molecules have evolved, the models suggested by MAGAT, STUART, BRIEGLEB, and the work done in this field by PAULING, are discussed. The features of a new calotte model, the EUGON set (of proper angles), are described. A treatment, with the help of the EUGON calotte set, of spatial arrangement problems of organic compounds is outlined. The role of calotte models in the treatment of theoretical problems of organic chemistry is defined, and the study, with the help of atom-calotte models, of energetics relevant to organic chemical compounds is demonstrated.

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