[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The Collision Areas of 1,3,5-Mesitylene and of the Most Highly Branched Heptanes

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A method previously given for matching molecule collision areas determined[2] experimentally by gaseous viscosity measurements with collision areas of probable models made to scale has now given consistently such successful results that it would seem that this type of approach could well be generalized to attack various problems of unknown or disputed spatial configuration of organic molecules, with the expectation of obtaining satisfying solutions. While, in the present paper, no attempt will be made to gain a decision between any disputed structures, some further evidence of the general trustworthiness of the method will be presented. We have chosen for examination two molecules which possess quite different collision areas, and which exhibit rather interesting features of structure in their spatial configuration, namely, 1,3,5-mesitylene and the most highly branched carbon chain of the heptane isomers (2,2,3-trimethylbutane).

First the data and the mathematical reduction of the data will be given, followed by a discussion of the results.

Experimental Procedure and Data

The viscosities of the two vapors were determined experimentally at several temperatures with the same apparatus and in precisely the manner already described.[2] The boiling points of mesitylene and of the heptane, the latter prepared synthetically according to the method[3] used by Edgar, Calingaert and Marker,[4] were, respectively, 164.5 and 80.2° (at 752 mm).

TABLE I

VISCOSITY DATA AND COLLISION AREA FOR MESITYLENE

Temp., °C.	η	η_c	Sutherland constant	Collision area (sq. Å.)
100.4[a]	0.725[b] × 10^{-4}	0.746 × 10^{-4}		43.03
150.4	.807[b] × 10^{-4}	.834 × 10^{-4}	136.3	42.2
200.0	.873[b] × 10^{-4}	.907 × 10^{-4}		42.1
			Av.	42.4

[a] This measurement at 100.4° was made by Dr. Ralph M. Melaven.

[b] The density of the liquid mesitylene at 65°, the temperature at which the mesitylene vaporized during the transpiration, was taken as 0.8265 [Perkin, *J. Chem. Soc.*, **69**, 1193 (1896)].

Calibration of the capillary with dry air gave the following results for the viscosity of air: at 24.2°, 182 × 10^{-6}; at 125°, 226 × 10^{-6}; at 200°, 256 × 10^{-6}.

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(1) Du Pont Fellow at The Ohio State University, 1931–1932.

(2) Melaven and Mack, THIS JOURNAL, **54**, 888 (1932).

(3) Chavanne and Lejeune, *Bull. soc. chim. Belg.*, **37**, 98 (1922).

(4) Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1483 (1929).

TABLE II

VISCOSITY DATA AND COLLISION AREA FOR 2,2,3-TRIMETHYLBUTANE

Temp., °C.	η	η_c	Sutherland constant	Collision area, sq. Å.
70.3[b]	0.729[a] $\times 10^{-4}$	0.734×10^{-4}		
101.1	.763[a]	.769	257	31.10
132.2	.820[a]	.827		31.08
176.1	.892[a]	.900		31.20
262.1	1.037[a]	1.048		31.10
				Av. 31.12

[a] The density of the liquid heptane at 22.5°, the temperature at which the heptane vaporized during transpiration, was taken as 0.6879 [Edgar and Calingaert, THIS JOURNAL, **51**, 1544 (1929)].

[b] In calculating the value of *C*, the Sutherland constant, the viscosity obtained at 70.3° was not used. High values for η are frequently found for temperatures close to the boiling point and have been ascribed to inexactness of the Sutherland equation at low temperatures [Rankine, *Proc. Roy. Soc.* (London), A88, 575 (1913)].

The experimental conditions were chosen so that the transpiration of the vapors through the capillary was slow enough to ensure viscous, and not permit turbulent, flow. The viscosities η at the several temperatures were calculated with Meyer's transpiration formula, as before, and were corrected for slip, η_c. Then the Sutherland constants were computed graphically and the collision areas calculated by means of Chapman's equation.

Discussion

Mesitylene.—For the shadow-graphic estimation of the average cross-sectional area of the mesitylene molecule, a model was made to scale (1 inch = 1 Å.), consisting of a flat graphite ring of six carbon atoms with diameters 1.42 Å. Three methyl groups were attached in the plane of the ring in the 1,3,5-positions. Three hydrogen atoms were also attached in the 2,4,6-positions, although as far as effect on the collision area is concerned the three hydrogens were completely buried underneath the larger methyl groups. The hydrogen atoms of the methyl groups were attached at tetrahedral angles, at internuclear C–H distances of 1.08 Å., and with a hydrogen domain radius of 0.72 Å. because of the probability that three hydrogen atoms on the average on one molecule bump three hydrogen atoms of another molecule in collision. The discussion of this point has already been given,[2] and in the construction of these models it is our consistent practice to assign hydrogen atom domain radii of 0.50, 0.65, 0.72 or 0.78 Å. when one, two, three or four hydrogen atoms, respectively, on a molecule partake in the collisional impact. Furthermore, since Pauling[5] has shown that the rotation of methyl groups around the C–C bond is easily excited, it is extremely probable that all three methyl groups on this molecule are spinning at the temperatures involved. A consideration of

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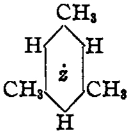
(5) Pauling, *Phys. Rev.*, **36**, 430 (1930).

the equipartition of energy principle and the moment of inertia of the methyl group, together with the average velocity of approach of bombarding molecules, shows that the methyl groups are undoubtedly spinning rapidly enough to present themselves as total rings of revolution. Similarly, it can be demonstrated that the spin of the molecule as a whole about the *z* axis, which passes through the center of the ring, and is perpendicular to the plane of the ring,  is rapid enough to produce effectively an almost total ring of revolution; although the spins about the other two rectangular axes, *x* and *y*, perpendicular to the *z* axis, are not sufficiently rapid to produce a *sphere* of revolution or in fact to affect the target area appreciably. The model of the electronic dome domain, the presence of which is due to the unsaturation of the benzene ring, was also attached to each face of the ring. The dome size (gas kinetic radius 2.0 Å.)[6] is, however, too small in comparison with the methyl rings to play anything but a minor part in producing the observed average collision area.

The average shadow area of this model ring of revolution (about the *z* axis) was then computed at forty-two different positions, separated from one another by approximately equal angles, as previously described.[2] The average collision area thus predicted for the molecule is 42.7. This is certainly in good agreement with the experimentally determined collision area of Table I.

Heptane, 2,2,3-Trimethylbutane.—Figure 1 shows an end view of the model of the branched heptane molecule. The spinning methyl groups M_1, M_2 and M_3 are attached at tetrahedral angles to carbon atom C_1. Directly behind C_1 is another carbon atom C_2 (not shown in drawing) to which are attached methyl groups M_4 and M_5 and hydrogen atom H, all at tetrahedral angles. A consideration of the moments of inertia about three different spin axes of the molecule taken as a whole, shows that the frequency of spin, compared with the average velocity of approach of bombarding molecules, is not sufficiently great to allow the molecule to present itself either as a sphere or as a cylinder of revolution. This justifies the procedure, then, of finding the average cross-sectional area of the static model by the shadow-graphic method.

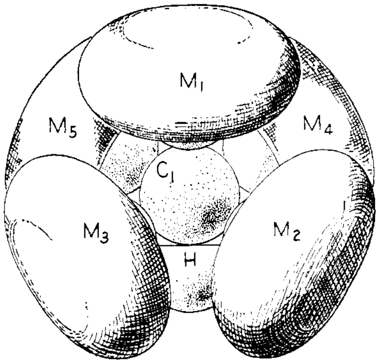


Fig. 1.

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(6) Mack, THIS JOURNAL, 54, 2141 (1932).

The average of forty-two different positions gives 29.5, on the assumption that *three* hydrogen atoms on each colliding molecule partake in an average collision. If *four* hydrogen atoms collide, on the average, the model collision area is 30.8. This again is in quite good agreement with the experimentally determined value of 31.1, in Table II.

In a previous paper[2] the collision area of the *n*-heptane molecule has been determined experimentally to be 26.7 sq. Å., and by an application of the shadow-graphic method the conclusion was reached that the *n*-chain is coiled up into a tight helix. In the present case the molecule is already bunched up by its structure into a compact, roughly spherical form, and its five spinning methyl groups give it a considerably larger collision area than that of the helical *n*-heptane. While the methyl groups themselves undoubtedly are spinning, it is not probable that the C_1 and C_2 carbon atoms can rotate on the bond which connects them. This is due to the size of, and manner of placement of, the methyl groups, the steric hindrance of which would prevent any such rotation. The same situation would exist in hexamethylethane.

Thus one would predict for these molecules, made up of isopropyl and tertiary-butyl groups, the same sort of isomerism recently observed for diphenyl, and one could easily proceed to the prediction of the possible isomers to be found, for example, for the di-halogen substitution products.

Summary

The viscosities of the vapors of 1,3,5-mesitylene and 2,2,3-trimethylbutane have been measured over a considerable temperature range, and the Sutherland constants and collision areas, respectively, 136.3 and 257, and 42.4 and 31.1 sq. Å., have been calculated from the data.

The shadow-graphically computed collision areas of the models made to scale, are 42.7 for mesitylene and 29.5 (or 30.8) for the heptane. These good matches between calculated and observed results are submitted as still further evidence for the reliability of this general method of determining spatial configuration of organic molecules.

A type of space isomerism similar to that found in diphenyl is predicted for 2,2,3-trimethylbutane and for hexamethylethane.

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