tion of helical molecules.[8] (3) The modification has greater $[\eta]$ values near 100% chloroform and greater k' values over the whole helical region than the enantiomorph, while in the coil region the curves are quite identical. Furthermore, by applying the molecular weight–intrinsic viscosity (in chloroform) relationship[9] for the enantiomorph it was found that a racemic modification shows the $[\eta]_{CHCl_3}$ value corresponding to a molecular weight approximately twice that of the enantiomorph of which it is composed. These results suggest that in solution in helix-forming media the enantiomorphic forms are in some way combined with each other and that the association of D-chain-L-chain is of higher order than that of L(or D)-chain-L(or D)-chain, provided k' gives a measure of association.

From the data presented we believe that the present polypeptide modification exists in solid and in solution not as a merely stoichiometric mixture of the two enantiomorphs but as a racemic compound. At present we have no evidence indicating that the formation of this macromolecular racemic compound is due to a side chain–side chain interaction between D- and L-polypeptide chains.[10]

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[8] P. Doty, J. H. Bradbury and A. Holtzer, *J. Am. Chem. Soc.*, **78**, 947 (1956).

[9] This was prepared, using several L-PMG samples, by correlating their intrinsic viscosities obtained in chloroform with the molecular weights estimated from light scattering data in DCA.

[10] M. Tsuboi, A. Wada and N. Nagashima, *J. Mol. Biol.*, **3**, 705 (1961).

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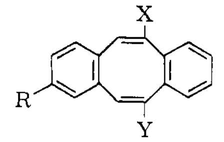
OPTICAL RESOLUTION OF A 1,2,5,6-DIBENZCYCLOÖCTATETRAENE DERIVATIVE

Sir:

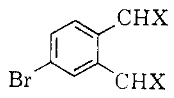
Cycloöctatetraene exists predominantly in the D_{2d} tub conformation.[1] The problem of electron delocalization in this and in the planar forms (D_{4h} or D_{8h}) continues to attract attention, as does the related question of the strain energy introduced in the conversion of the tub into the planar forms.[2]

Racemization studies on dissymmetric cyclooctatetraene derivatives could lead to an experimental estimate of the energy difference between tub and planar (transition state) conformations and would therefore be of considerable interest. Nevertheless, no optically active compound in this class has heretofore been reported, even though it was recognized by Cope, *et al.*,[3] and by Pechet[4] that nonplanarity could in principle be demonstrated by the optical resolution of mono-substituted cyclooctatetraenes[3] and of dibenzcycloöctatetraenes of formula Ia.[4] We now wish to report the first resolution of a substituted cycloöctatetraene derivative, the dibenzcycloöctetraene Ib.

Irradiative bromination of 4-bromo-*o*-xylene gave IIa, m.p. 113–115°, which was hydrolyzed (fuming sulfuric acid) to IIb, m.p. 98–100°. Condensation with *o*-phenylenediacetonitrile to Ic, m.p. 242–244°, followed by hydrolysis (phosphoric–acetic acid mixture), gave Ib, m.p. 290–292° (dec.). All compounds gave satisfactory elemental analyses for carbon, hydrogen, bromine and (in the case of Ic) nitrogen. Resolution *via* the brucine salt gave optically active enantiomers of Ib, $[\alpha]^{21}\text{D} + 71.2°$ and $[\alpha]^{26}\text{D} - 61.6°$ (c 0.9, ethanol).



Ia, $X \neq Y$, $R = H$
b, $X = Y = COOH$, $R = Br$
c, $X = Y = CN$, $R = Br$
d, $X = Y = H$, $R \neq H$



IIa, $X = Br_2$
b, $X = O$

Solutions of the compound which were allowed to stand for at least eight weeks at room temperature exhibited no loss of optical activity. However, at elevated temperatures the interconversion of enantiomers (Fig. 1) becomes an important process.

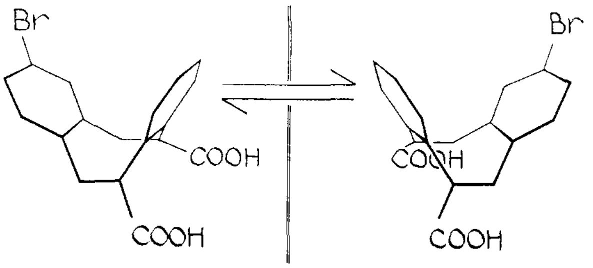


Fig. 1.

In preliminary experiments we have found that Ib in diethylene glycol diethyl ether racemizes at 120, 130 and 140° with a half-life of approximately 140, 62 and 25 minutes, respectively. The estimated E_{act} is 27 kcal./mole. The calculated pre-exponential term (10^{11} sec.$^{-1}$) falls well within the range of values (10^{10} to 10^{13} sec.$^{-1}$) most frequently reported for the common optically labile atropisomers, such as the biphenyls.[5]

The demonstrated potential barrier is recognized to be an *upper limit* for cycloöctatetraene. The presence of the two benzene rings undoubtedly minimizes any effect of π-electron delocalization on the stabilization of the planar transition state, relative to the nonplanar ground state: such an effect could possibly be an important factor in the conversion of cycloöctatetraene to the planar forms.[2] In addition, inspection of models reveals that non-

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[2] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 10.7; G. Ahlers and J. F. Hornig, *J. Phys. Chem.*, **65**, 2102 (1961); C. A. Coulson, *Tetrahedron*, **12**, 193 (1961); N. L. Allinger, *J. Org. Chem.*, **27**, 443 (1962); F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962); T. J. Katz, W. H. Reinmuth and D. E. Smith, *ibid.*, **84**, 802 (1962); O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962); C. A. Coulson and W. T. Dixon, *ibid.*, **17**, 215 (1962).

[3] A. C. Cope and M. R. Kinter, *J. Am. Chem. Soc.*, **73**, 3424 (1951); A. C. Cope, M. Burg and S. W. Fenton, *ibid.*, **74**, 173 (1952).

[4] M. M. Pechet, Ph.D. Dissertation, Harvard University, 1944; *cf.* also L. F. Fieser and M. M. Pechet, *J. Am. Chem. Soc.*, **68**, 2577 (1946).

[5] D. M. Hall and M. M. Harris, *J. Chem. Soc.*, 490 (1960).

bonded interaction of carboxyl groups and benzene hydrogens in the transition state is likely to contribute significantly to the destabilization of the transition state. Work is in progress to settle this question by studies of the resolvability (and optical stability) of Id and of other dissymmetric cyclooctatetraenes.

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NEGATIVE TEMPERATURE COEFFICIENTS FOR ION-MOLECULE REACTIONS

Sir:

Stevenson and Schissler[1,2] observed a "small but real" negative temperature coefficient for the cross-section of reactions between hydrocarbon ions and molecules. The phenomenological cross-section is inversely proportional with the repeller field strength in these cases. Gioumousis and Stevenson[2] calculated also the relation between the phenomenological cross-section Q and the microscopic cross-section σ for reactions between molecular ions and molecules when the rate of reaction is determined only by the interaction between a charge and an induced dipole, *i.e.*, when σ is inversely proportional to the relative velocity g at a large distance between ion and molecules. In this case Q is found to be inversely proportional to the square root of the repeller field strength, and independent of temperature.

It has been pointed out by Hamill and Boelrijk[3,4,5,6] that a variation of Q inversely proportional to the repeller field strength occurs when the average value of σ for velocities of the ion at the exit slit is practically zero. It also has been found experimentally that σ for ion–molecule reactions in cyclopropane[4] and in neopentane[5,6] can be described adequately by functions of the form $\sigma(\epsilon) = \sigma_1\epsilon^{-1/2} - \sigma_H$, for $\epsilon \leqslant \epsilon_c$ and $\sigma(\epsilon) = 0$ for $\epsilon \geqslant \epsilon_c$, where ϵ is the kinetic energy of the ion, and ϵ_c, σ_1 and σ_H are constants. This suggests that $\sigma(g) = (g_c/g - 1)\sigma_H$ for $g \leqslant g_c$ and $\sigma(g) = 0$ for $g \geqslant g_c$ is a suitable model. The constant σ_1 is presumably equal to the cross-section for a collision in the ion induced dipole model at 1 eV. relative kinetic energy multiplied by an efficiency factor for the reaction under consideration. The physical meaning of σ_H is not clear, though it may be related to nearly head-on collisions.

An examination of Gioumousis and Stevenson's derivation shows that no temperature effect occurs, if the product $g\sigma(g)$ is a constant. An example will be given that a negative temperature coefficient can be found for the phenomenological cross-section without introducing a temperature effect in the microscopic cross-section when $g\sigma(g)$ is a decreasing function of g.

We considered the trajectories of two ions starting with equal velocities but in opposite direction from a point in the plane of the mass spectrometer electron beam. These trajectories are parts of a parabola. The trajectories can be replaced by the trajectories of two hypothetical ions starting in the top of the parabola, with the same velocity components as the former ions in directions perpendicular to the repeller field and no velocity in the direction of the field. This replacement is allowed if the number of primary ions does not change appreciably due to reactions. The influence of the initial velocity distribution in the direction of the field will be found back in the upper limit of the integral over the trajectories of the ions within the ionization chamber. This influence will be neglected as the contribution to the reaction is very small when the velocity of the ion in the laboratory reference system is much larger than g_c.

The sixfold integral which has to be evaluated becomes now

$$i_s/i_p = N \int \sigma(g) f_{x1} f_{y1} f_{x2} f_{y2} f_{z2} \mathrm{d}v_{x1} \mathrm{d}v_{y1} \mathrm{d}v_{x2} \mathrm{d}v_{y2} \mathrm{d}v_{z2} \mathrm{d}s$$

where f_{x1} is the Maxwell–Boltzmann distribution function of the velocity v_{x1} of the ion in the x direction, *etc.* The indices 1 and 2 are used to indicate, respectively, the ion and the molecule; the homogeneous electric field is taken in the z direction; i_p and i_s are, respectively, the primary and secondary ion current; ds is an element of the relative path of an ion–molecule pair[7]) and N the density of the molecules.

Taking $\sigma(g) = C_1/g$, it is easily derived that

$$Q = i_s/i_p \times 1/Nd_0 = C_1(2m_1/eEd_0)^{1/2}$$

which is equivalent to Gioumousis' expression (17).[2] E is the electric field strength and d_0 is the distance between electron beam and exit slit.

Evaluation of the integral for $\sigma(g) = (g_c/g - 1)\sigma_H$ yields

$$Q = \frac{2kT}{eE_0d_0}\,\frac{m_1}{\mu}\,\sigma_H \left\{ \frac{1}{2}w^2 - \int_0^w e^{-y^2}\mathrm{d}y \int_0^y e^{x^2}\,\mathrm{d}x \right\}$$

where the dimensionless quantity w is given by $w = (\mu/2kT)^{1/2}g_c$. Tables of the value of the integral as function of w have been published.[8]

The temperature effect can be found by calculating Q at different temperatures. The results of such calculations for $eEd_0 = 2$ eV. and for three reactions are presented in the table.

Reaction	σ_1 (eV.$^{1/2}$Å.^{2})	σ_H (Å.^{2})	T (°K.)	Q (Å.^{2})
$C_2H_4^+ + C_2H_4$[a]	49.2	40.0	400	26.8
			500	26.3
			600	25.6
$CH_3OH^+ + CH_3OH$[a]	42.8	49.4	400	14.8
			500	14.3
			600	13.7
$CS_2^+ +$ neo-C_5H_{12}[b]	5.3	3.1	400	0.422
			500	0.420
			600	0.413

[a] Estimated, see p. 35 of ref. 6; no efficiency factor f taken into account. The relative change of Q with temperature does not depend on f, unless f changes with temperature. [b] Measured, see p. 106 of ref. 6.

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