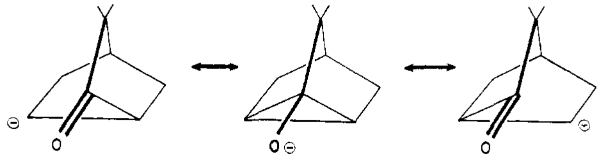
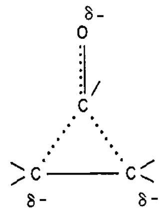
and trideuterated species as well as undeuterated material. After a 100 hr. run there was a slight indication (0.2%) of a tetradeuterated species as well. When the product from the 100 hr. run was treated with potassium *t*-butoxide in fresh *t*-butyl alcohol-*d* for an additional 166 hr., the relative amounts of deuterated species were: 1% (no D), 7% (1D), 26% (2D), 38% (3D), 21% (4D), 6% (5D), 1% (6D). Incorporation of up to three deuterium atoms is understandable in terms of the homoenolate anion II, which could permit exchange of both hydrogens at C.6 as well as of the bridgehead hydrogen at C.1. This latter hydrogen becomes exchangeable as a consequence of the interconversion of positions 1 and 6 in the homoenolate anion. That prolonged treatment eventually produced species with more than three deuterium atoms shows that C.6 is not the only homoenolizable site.

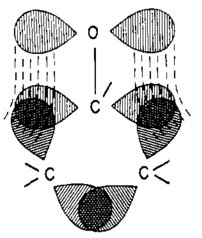
Additional information on the homoenolate ion was obtained by comparison of the extent of racemization of (+)-camphenilone with its extent of deuterium incorporation. Table II shows the results of four runs conducted with *t*-butoxide at 185° in *t*-butyl alcohol-*d*. The deuterium incorporation was assayed mass spectroscopically and the extent of racemization was determined from the optical activity of the derived semicarbazone. In each run the percentage racemization corresponded closely with the percentage of molecules having deuterium.[4] This close correspondence between racemization and deuterium entry reveals (a) that the first hydrogen exchanged is at a location that leads to a racemizable ion (this can only be at C.6); and (b) that the homoenolate ion formed by loss of a C.6 hydrogen racemizes before it can pick up deuterium from the solvent. Consequently, the homoenolate anion either has a symmetrical structure or, if unsymmetrical, it rearranges to its enantiomer faster than it reverts to the ketone. The symmetrical ion may be described approximately by the three canonical structures IIIa, b, c,[5] or by either of the mesomeric formulations IVa or IVb (shown as partial structures).



IIIa IIIb IIIc



IVa



IVb

TABLE II

Time, hr.	% Molecules with— No D	One or more D	% Racemized
12	75	25	26
24	48	52	52
36	29	71	69
48	13	87	88

These results reveal the existence of homoenolate anions and bring into consideration the general concept of homoenolization. This concept may be extendable to transformations of biological interest, to sulfur and phosphorus compounds (*e.g.*, sulfones, phosphine oxides), to polyfunction molecules, *etc.*, and work along these lines is in progress.

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(4) An equivalent statement is that the fraction of molecules not racemized corresponds to the fraction that contains no deuterium.

(5) If the ion can have an unsymmetrical structure then IIIa and IIIb could differ slightly in geometry, in which case the resonance arrows would be replaced by equilibrium arrows.

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RECEIVED OCTOBER 15, 1962

INHERENTLY DISSYMMETRIC CHROMOPHORES: THE ABSOLUTE CONFIGURATION OF (−)-*trans*-CYCLOÖCTENE

Sir:

It is recognized that the contribution to a transition moment associated with the oscillation of charge between 2p orbitals positioned on two separate atomic centers can be either electric dipole allowed-magnetic dipole forbidden, or magnetic dipole allowed-electric dipole forbidden, depending on whether the orbitals are directed parallel or perpendicular to each other, as indicated in I and II, respectively. Any conformation in which the orbitals are mutually disposed at some intermediate relative angle γ (*e.g.*, III) may be viewed as a superposition of I and II. In such circumstances the transition moment can be both electric and magnetic dipole allowed, and the relevant electric and magnetic transition moment contributions are directed collinearly. More specifically, for an angle of twist γ, situation I contributes to the extent cos γ and situation II to the extent sin γ, so that the contribution to the rotational strength associated with situation III will be proportional to sin γ cos γ or to sin 2γ. Evaluation of the relevant matrix elements indicates that a (+)-sign is to be associated with the chirality indicated by III.[1] Hence any transition involving such a conformation of orbitals may be viewed as arising from an inherently dissymmetric chromophore whose transitions are perforce optically active. Such a situation would arise in the case of an olefin containing a twisted ethylenic bond and would manifest itself experimentally by a marked increase in the magnitude of the optical activity (relative to that of comparable but unstrained olefins) as measured in the visible and near ultraviolet.

In light of the above discussion, the molecule (−)-*trans*-cycloöctene[2] ($[\alpha]^{29}_{D}$ −411° or molecular

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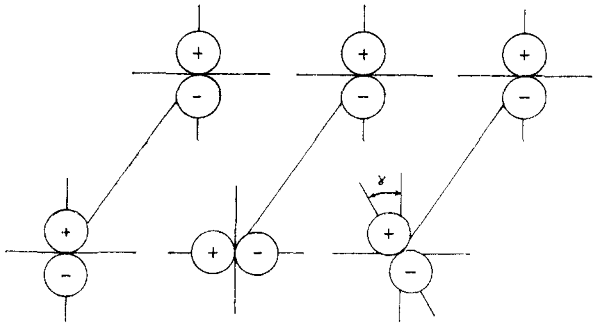
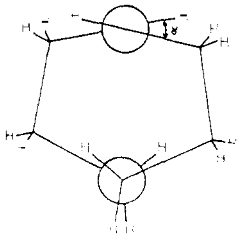
(1) R. Deen, Dissertation, Leiden, 1961.

(2) A. C. Cope, C. R. Ganellin and H. W. Johnson, Jr., *J. Am. Chem. Soc.*, **84**, 3191 (1962).

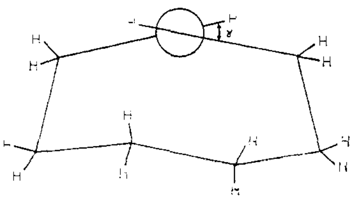


I II III

rotation $[\phi]^{29}_D$ −453°, methylene chloride), where Dreiding models indicate a permanent twist of the double bond,[3] is of special interest. The Dreiding models in fact suggest two conformations of minimum angle strain which are indicated schematically in Newman projections in IV and V. The angle of twist γ may actually be slightly different for the two conformers, although the models indicate that γ is substantially the same in the two cases.



IV



V

Employing the simplest Pariser–Parr[4] wave functions for ethylene in conjunction with the Rosenfeld equation,[5] one arrives at an expression for $[\phi_t]$, the contribution of a twisted ethylenic bond to the molecular rotation

$$[\phi_t] = \frac{96\pi N_0}{hc}\,\frac{\nu^2}{\nu_0^2-\nu^2}\,\frac{n^2+2}{3}\,R_{45}\sin 2\gamma \qquad (1)$$

where R_{45} is the maximal rotational strength (for a given bond distance and transition frequency ν_0) associated with $\gamma = 45°$. Here N_0 is Avogadro's number, and h, c, and n have their usual meanings. For $\gamma = 15°$, the Pariser–Parr type calculations indicate that the first ethylene π–π^* singlet transition would shift in the vapor phase from 7.6 ev. (163 mμ) to 7.38 ev. (168 mμ). Assuming a similar red shift for IV and V relative to *trans*-2-butene (λ_{max}^{vapor} 178 mμ),[6] and assuming no further shift for the solution spectrum, one calculates from equation (1) values of $[\phi_1]^{29}_D$ 395° and 404° for isoöctane and methylene chloride solvents, respectively. The optical activity so calculated is a somewhat sensitive function of angle, and for $\gamma = 20°$ one calculates $[\phi_t]^{29}_D$ 551° and 564°, respectively, for the two solvents. If it is allowed that the inherent dissymmetry associated with the twist of the double bond accounts for the major portion of the observed optical activity[7] at 589 mμ, one may conclude that the absolute configuration of the (−)-enantiomer is as shown in IV and V.[8]

A direct quantitative comparison of the calculated values for $[\phi_t]_D$ with experimental values of $[\phi]_D$ is unwarranted because of the uncertainty in ν_0 and the contributions of higher lying transitions to $[\phi]_D$. Rather, a direct comparison of the calculated with the experimental rotational strength (presently lacking) for the lowest π–π^* singlet would be more appropriate. Nevertheless, if we estimate an upper limit of ± 140° due to these uncertainties,[9] we may still specify γ as equal to 17 ± 5°.

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[3] The possibility of a twisted double bond in *trans*-cycloöctene has been considered previously in connection with the interpretation of dipole moment data; N. L. Allinger, *J. Am. Chem. Soc.*, **80**, 1953 (1958).

[4] R. G. Parr and R. Pariser, *J. Chem. Phys.*, **23**, 711 (1955), sections IVA and B.

[5] L. Rosenfeld, *Z. Physik*, **52**, 161 (1928).

[6] J. T. Gary and L. W. Pickett, *J. Chem. Phys.*, **22**, 599 (1954).

[7] Clearly the inherently dissymmetric twisted double bond is situated in a molecular environment which is itself dissymmetric. The approximation of the present work is to ignore the weakly perturbing effects of such an environment on the ethylenic chromophore which would in a higher order approximation provide further smaller contributions to the optical activity and also affect the dipole moment (*cf.* ref. (3)).

[8] According to the nomenclature proposed by R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956), the configuration of IV and V is (*S*) if the double bond is taken as the axially asymmetric frame of reference (as in allenes, biphenyls and the like).

[9] The estimate of ±140° is based in part on the assumption that the twisted six-carbon methylene chain contributes relatively little to the observed rotation at 589 mμ, as might be inferred from the values of $[\phi]_D$ generally reported for flexible hydrocarbons. Recently P. Pino and G. P. Lorenzi (*J. Am. Chem. Soc.*, **82**, 4745 (1960)) and W. J. Bailey and E. T. Yates (*J. Org. Chem.*, **25**, 1800 (1960)) have shown that certain poly-α-olefins may exhibit enhanced rotations ($[\alpha]_D$ 200–300°) and the phenomenon has been attributed to stereoregularity in the relevant alkane polymers. Dr. Edel Wasserman points out to us (and we concur in his opinion) that comparable enhancements could conceivably be associated with the more or less rigidly fixed methylene chain in IV and V. In this event, the 10° range of uncertainty for γ would necessarily have to be widened. However, in order that our claims as to absolute configuration be invalidated, the contribution to $[\phi]_D$ associated with the methylene chain would have to exceed 400°, and this we deem unlikely.

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ISOMERIZATION AS A PRIMARY PROCESS IN THE PHOTOLYSIS OF CROTONALDEHYDE

Sir:

Previous work on the photolysis of crotonaldehyde has not led to any very definite conclusions about the mechanism of the reaction. Though Blacet and Roof[1] in an early publication stated that no photo-decomposition occurred, later studies[2,3] showed clearly that free radicals were produced and that CO and propylene were the main products. A more recent study[4] of the Hg-photosensitized decomposition of crotonaldehyde confirmed the earlier observations that propylene was a major product and that the reaction produced the propenyl radical. Our recent studies of the photolysis of crotonaldehyde in the gas phase at ~30° in the wave length range 2450–4000 Å.

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[1] F. E. Blacet and J. G. Roof, *J. Am. Chem. Soc.*, **58**, 73 (1936).

[2] F. E. Blacet and J. E. Lu Valle, *ibid.*, **61**, 273 (1939).

[3] D. H. Volman, P. A. Leighton, F. E. Blacet and R. K. Brinton, *J. Chem. Phys.*, **18**, 203 (1950).

[4] A. G. Harrison and F. P. Lossing, *Can. J. Chem.*, **37**, 1696 (1959).