

A complete X-ray investigation of trisalicylide is being undertaken by Dr. H. F. Kay, of the H. H. Wills Physical Laboratory of this University. The molecule of trisalicylide is mobile, and is structurally related to that of *symm*-tribenzcycloodecatriene<sup>2</sup>; some of the configurations which could be assumed by this type of molecule have already been illustrated<sup>2</sup>.

There is thus only one known disalicylide, and its high dipole moment (see following letter) proves that it possesses the folded *cis* form (as *Ib*) in which the strain is minimal. Disalicylide, therefore, is a *cis* molecule and *symm*-dibenzcyclooctadiene a *trans* molecule of the type under discussion; but no case is yet proved of a single substance of this kind existing in both *cis* and *trans* forms. Stereoisomerides are being sought of these and structurally related molecules, including the disulphonylides (O.C<sub>6</sub>H<sub>4</sub>.SO<sub>2</sub>)<sub>2</sub> and the di-anthranilides (NH.C<sub>6</sub>H<sub>4</sub>.CO)<sub>2</sub>. The configuration of *symm*-dibenzcyclooctatetraene<sup>6</sup>, the diolefinic analogue of (I), is not known, but it must almost certainly be the *cis* form (as *Ib*); if so, catalytic reduction which gives *trans-symm*-dibenzcyclooctadiene<sup>6</sup> (*Ia*) is accompanied by a change of configuration, but rupture of a C—C bond is not necessarily involved. Tetra-benzcyclooctatetraene (tetraphenylene) has been shown to possess the wholly *cis* configuration of the cyclooctatetraene ring<sup>7</sup>.

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<sup>1</sup> Private communication to Anschutz, R.; see Richter-Anschutz, "Chemie der Kohlenstoffverbindungen", 2, Pt. 2, 393 (12th edit., 1935).

<sup>2</sup> *J. Chem. Soc.*, 27 (1945).

<sup>3</sup> *J. Chem. Soc.*, 891 (1948).

<sup>4</sup> *Berichte*, 52, 1880 (1919); later references to the disalicylides are ref. 5 and Anschutz, R., *J. Pract. Chem.*, 105, 158 (1922); Anschutz, R., and Rippenkröger, K., *Annalen*, 439, 4 (1924); Anschutz, L., and Neher, R., *J. Pract. Chem.*, 159, 264 (1941); Kohlrausch, K. W. F., *J. Pract. Chem.*, 159, 268 (1941); Anschutz, L., and Mayer, A., *J. Pract. Chem.*, 159, 343 (1942); Kahovec, L., and Kohlrausch, K. W. F., *Monatsh.*, 74, 333 (1943); Anschutz, L., and Neher, R., *Berichte*, 77, 634 (1944); Anschutz, L., and Gross, G., *Berichte*, 77, 634 (1944).

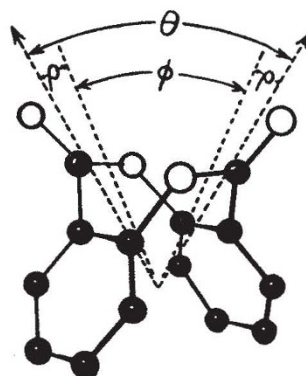
<sup>5</sup> *Berichte*, 52, 2227 (1919).

<sup>6</sup> Fieser, L. F., and Pechet, M. M., *J. Amer. Chem. Soc.*, 68, 2577 (1946).

<sup>7</sup> Karle, I. L., and Brockway, L. O., *J. Amer. Chem. Soc.*, 66, 1974 (1944).

### Dipole Moments of the Salicylides

THE electric dipole moments of the  $\alpha$ - and  $\beta$ -salicylides (assumed to be disalicylides) were found to be 6.27 and 2.42 D. respectively in benzene solution. The solutions showed no change of polarization with time. The former, being definitely a disalicylide, may therefore be given the *cis* configuration (cf. *Ib* above). Baker, Banks, Lyon and Mann<sup>1</sup> have shown that the geometry of this form of ring is variable, but the configuration (*Ib*) is the most likely because the resonance energy will then be a maximum (cf. Marsden and Sutton<sup>2</sup>). The moment of the compound should then be approximately the resultant of the two lactone group moments (each of 4.12 D.<sup>3</sup>) at an angle  $\theta$ , which can be calculated if the angles  $\phi$  and  $\rho$  are known (see diagram). The angles Ph—C—O and Ph—O—C may each be assumed to lie between the limits of 109.5° and 120°. Since the rest of the geometry of the molecule is determined by the benzene rings,  $\phi = 64.5$ –70.5°.  $\rho$  may be obtained from a molecular-orbital calculation<sup>4</sup> and is found to be c. 27°.  $\theta$  is therefore 82–86°, and the calculated moment is 6.2–6.0 D.



The moment of the  $\beta$ -compound is too large for the *trans* configuration of the disalicylide ring, even though atom polarization might give rise to a considerable apparent moment<sup>4,5</sup>; but the observation (*vide supra*) that the compound is trisalicylide makes an explanation possible. The observed moment now becomes 2.97 D. Of the configurations shown by Baker *et al.*<sup>1</sup> for a similar ring system, the moment of 2 A. is likely to be too small and that of 2 D. may be much too large; the compound probably exists mainly in configurations more closely allied to 2 B. and 2 C. In these the lactone groups can be nearly coplanar without getting in each other's way.

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<sup>1</sup> Baker, W., Banks, R., Lyon, D. R., and Mann, F. G., *J. Chem. Soc.*, 28 (1945).

<sup>2</sup> Marsden, R. J. B., and Sutton, L. E., *J. Chem. Soc.*, 1383 (1936).

<sup>3</sup> Orgel, L. E., private communication.

<sup>4</sup> Coop, I. E., and Sutton, L. E., *J. Chem. Soc.*, 1269 (1938).

<sup>5</sup> Davidson, N. R., and Sutton, L. E., *J. Chem. Soc.*, 347 (1939).

### Mesomeric Polarizations of Ketens

SINCE the literature contains only one experimental determination of the dipole moment of a keten derivative, namely, that by Hannay and Smyth<sup>1</sup> of the parent member of the series, studied as a gas, we desire to record the following results obtained from solutions in benzene at 25°. They represent part of a programme which has had to be interrupted and cannot be resumed for some time.

	Total Pn. at infinite dil.	Molecular refraction	Apparent moment
Diphenylketen	138 c.c.	62 c.c.	1.9 <sub>8</sub> D
Mesitylphenylketen	143 c.c.	73.5 c.c.	1.8 <sub>8</sub> D
Dimethylketen	91 c.c.	20.2 c.c.	1.8 <sub>8</sub> D

It will be noted that in the three instances for which comparable figures now exist, the moment of the keten is less than that of its related ketone.

	Parent	Dimethyl-	Diphenyl-
Keten	1.45 <sup>1</sup>	1.8 <sub>8</sub>	1.9 <sub>8</sub>
Ketone	2.27 <sup>2</sup>	2.7 <sub>4</sub> <sup>3</sup>	3.0 <sup>3</sup>
$\delta\mu$	-0.8	-0.9	-1.1

Further,  $\delta\mu$  is of the same order for each pair. The existence of such permanent reversed polarizations, acting in opposition to those expected for an unperturbed carbonyl-containing structure, was explicitly forecast by Ingold<sup>4</sup> in 1934, when he formulated mesomeric states for 1:2-dienes generally as

