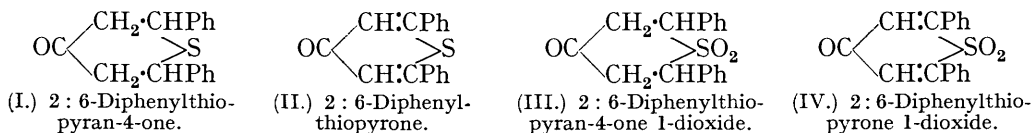


133. Studies in Dielectric Polarisation. Part XII. Dipole Moments and Structure of Thiopyrones and Related Compounds.

By F. ARNDT, G. T. O. MARTIN, and J. R. PARTINGTON.

IN Part V (J., 1933, 87) the dipole moments of some pyrone compounds were recorded. The present part describes the moments of the compounds (I)—(IV). The highly purified



specimens used for the measurements were prepared as described by Arndt and co-workers (*Ber.*, 1925, 58, 1633), except that the bromination of (III) was carried out in warm glacial acetic acid solution instead of chloroform, from which there is a tendency for the monobrominated derivative to separate. [For the *cis*- and *trans*-forms of (I), cf. *Ber.*, 1930, 63, 313.]

These compounds are of interest from the point of view of dipole-moment measurement in relation to the constitution of pyrones, which has been discussed for many years. A summary of the earlier literature on these compounds is given in Part V (*loc. cit.*), where values for the dipole moments of 2 : 6-dimethylpyrone, 2 : 6-diphenylpyrone, and 2 : 6-dimethyl-4-thiopyrone are given.

EXPERIMENTAL.

The apparatus used for dielectric-constant measurements, which was designed in collaboration with Mr. E. G. Cowley, was a modification of that described previously (J., 1932, 2812). The heterodyne-beat method is employed, a valve-maintained quartz crystal being used for one of the oscillators. The second oscillator was tuned by a Muirhead standard variable air condenser of 150 $\mu\mu\text{F}$ capacity, which could be increased by connecting a fixed air condenser of 100 $\mu\mu\text{F}$ capacity in parallel with it. Both condensers had National Physical Laboratory calibrations accurate to 2 parts in 10,000, and, by means of the worm drive with which it was fitted, the variable condenser could easily be read to 1 part in 10,000. The lead-covered cable which was previously used for the leads to the variable condenser was replaced by a copper rod supported by bakelite bushes inside a stout copper tube, this tube forming the earthed conductor.

The dielectric cell was of the type described by Henriquez (*Physica*, 1933, 1, 41), modified so that it could also serve as a pyknometer. Its capacity was 40 $\mu\mu\text{F}$, and weight about 55 g., 15 c.c. of solution being required to fill it.

The benzene used for the solutions was purified in the usual manner (see Part VIII, J., 1933, 1252).

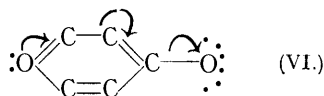
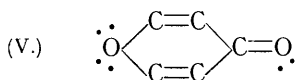
Results.—The electronic polarisations P_E of the compounds were calculated (as in Part V) from the sum of the atomic refractions. The moments were calculated as in the previous papers of this series. All moments are given in Debye units (10^{-18} e.s.u.).

2 : 6-Diphenylthiopyran-4-one					2 : 6-Diphenylthiopyrone 1-dioxide, m. p. 144°.				
<i>cis</i> -Form, m. p. 113°.					<i>trans</i> -Form, m. p. 87°.				
f_2 .	d_{40}^{20} .	ϵ .	P_{12} , c.c.	P_2 , c.c.	f_2 .	d_{40}^{20} .	ϵ .	P_{12} , c.c.	P_2 , c.c.
0.00000	0.8788	2.277	26.55	—	0.00000	0.8788	2.277	26.55	—
0.00933	0.8873	2.320	27.51	129.0	0.01118	0.8877	2.330	27.75	133.5
0.01248	0.8893	2.332	27.82	127.9	0.01537	0.8907	2.348	28.18	132.8
0.01536	0.8916	2.342	28.07	125.4	0.01967	0.8945	2.367	28.63	132.2
0.01847	0.8941	2.352	28.35	124.1	0.02519	0.8984	2.389	29.19	131.3
$P_{2\infty} = 135.6$ c.c.; $P_E = 78.8$ c.c.; $\mu = 1.64$ D.					$P_{2\infty} = 135.35$ c.c.; $P_E = 78.8$ c.c.; $\mu = 1.62$ D.				
2 : 6-Diphenylthiopyrone, m. p. 132°.					2 : 6-Diphenylthiopyrone 1-dioxide, m. p. 144°.				
0.00000	0.8788	2.277	26.55	—	0.00000	0.8782	2.274	26.51	—
0.00954	0.8872	2.554	30.71	462.5	0.01663	0.8960	2.328	27.98	114.85
0.01371	0.8911	2.666	32.31	446.2	0.01930	0.8987	2.336	28.21	114.76
0.02028	0.8969	2.847	34.77	431.6	0.02390	0.9036	2.351	28.61	114.70
0.02257	0.8987	2.910	35.61	427.7					
$P_{2\infty} = 486$ c.c.; $P_E = 78.4$ c.c.; $\mu = 4.39$ D.					$P_{2\infty} = 115.2$ c.c.; $P_E = 86.3$ c.c.; $\mu = 0.93$ D.				

DISCUSSION OF RESULTS.

For 2 : 6-diphenylthiopyrone (II), the calculated moment based on the formula (II), any interaction through the double bonds being neglected, is the difference between the moments of the $\text{C} \begin{smallmatrix} \curvearrowright \\ \curvearrowleft \end{smallmatrix} \text{C}=\text{O}$ and the $\text{C} \begin{smallmatrix} \curvearrowright \\ \curvearrowleft \end{smallmatrix} \text{S}$ group. The moments of benzophenone (3.0 *D*) and of diphenyl sulphide (1.5 *D*) being taken for these, the calculated moment is about 1.5 *D*, whereas the observed value is 4.4 *D*. Considerable interaction through the double bonds is thus indicated. In (I) the absence of the double bonds excludes the possibility of rearrangement occurring. From the difference between the moments of acetone (2.75 *D*) and of diethyl sulphide (1.57 *D*), the calculated moment is 1.18 *D*. Since this saturated ring is probably flexible, this can be considered to be in agreement with the value 1.6 *D* observed for both the *cis*- and the *trans*-form.

For (IV) the moment is calculated by taking the difference between those of the $\text{C} \begin{smallmatrix} \curvearrowright \\ \curvearrowleft \end{smallmatrix} \text{C}=\text{O}$ and the $\text{C} \begin{smallmatrix} \curvearrowright \\ \curvearrowleft \end{smallmatrix} \text{S} \begin{smallmatrix} \curvearrowright \\ \curvearrowleft \end{smallmatrix} \text{O}$ group. If the moments of benzophenone (3.0 *D*) and diphenylsulphone (5.1 *D*), respectively, are taken for these, the calculated moment is 2.1 *D*, while the value observed is 0.93 *D*. Obviously, this compound behaves in an entirely different manner from (II). Rearrangement of the double bonds cannot occur, since the lone pairs of electrons of the sulphur atom are no longer present, having been donated to the two oxygen atoms in the formation of the sulphone group. No electronic drift round the ring can take place, and the tendency for the two ends of the ring to become oppositely charged is no longer present. It need hardly be said that the migration of complete electrons in (II) is not permissible, since the molecule thus formed would have a very large moment (about 20 *D*), and such a migration has never been assumed either in this series of papers or in the earlier papers of one of the authors (Arndt, *Ber.*, 1924, 57, 1906; 1930, 63, 2963). The latter considered the actual state of the molecules of γ -pyrones and thiopyrones as lying "in between" the two states expressed by the unsaturated ketonic and the betainic formula, such "intermediate state" being interpreted as the time-integral of a very rapid electronic oscillation between the two states, the state corresponding to formula (II) being predominant. A similar view has recently been expressed by Sutton (Faraday Society Discussion on Dipole Moments, 1934), who explains the fact that pyrones do not possess such a large moment as complete ionisation would indicate, by assuming



resonance between the two forms (V) and (VI), the first structure being the more important ; a similar explanation for the thiopyrones is offered.

The dipole moment of 2 : 6-diphenylthiopyrone 1-dioxide (IV) is lower than the calculated value. This may perhaps be due to some effect of the double bonds, which is present in the case of thiophen ($\mu = 0.63$ *D*; Hassel and Naeshagen, *Tids. Kjemi*, 1930, 10, 81), the moment of which is much lower than that of an aliphatic sulphide, *e.g.*, diethyl sulphide ($\mu = 1.57$ *D*; Part I, J., 1931, 2062). Another example of this effect is provided by furan ($\mu = 0.63$ *D*; Part I, *loc. cit.*), the moment of which is also much smaller than that of an aliphatic ether, *e.g.*, diethyl ether ($\mu = 1.22$ *D*; Krchma and Williams, *J. Amer. Chem. Soc.*, 1927, 49, 2408). These low values cannot be completely explained by widening of the valency angle, since this assumption (Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, 54, 3230) leads to improbably large values for the valency angles.

The solubility of 2 : 6-diphenylthiopyran-4-one 1-dioxide (*cis*-form) (III) in benzene at 20° was too small to allow of a measurement being taken. The only suitable solvent found was dioxan, and measurements then indicated a large moment (about 3 *D*), but it appeared that some action between the compound and the solvent can occur. The solution on keeping changed from colourless to pale yellow, and later deposited a slight brownish-purple precipitate, the amount of which had become appreciable after 2 or 3 days. Distil-

lation of the dioxan under reduced pressure (2—3 cm.) left a yellowish residue, but on refluxing with benzene the colour practically disappeared, and the compound crystallised perfectly colourless and with an m. p. identical with that of the original specimen. A small quantity of yellow substance remained on the sides of the dish, and the m. p. of the last portion recovered was depressed.

Although no definite significance can be attached to the measurements in dioxan solution, the compound (III) might, by calculation, be expected to have a moment of about 2 *D*, *i.e.*, greater than that observed for the compound (IV).

Further information is provided by measurements of the heats of combustion of these compounds (Lorenz and Sternitzke, *Z. Elektrochem.*, 1934, **40**, 501). Details of these experiments are to be published elsewhere, and we have to thank Dr. Lorenz for permission to reproduce the following data for the molecular heats of combustion (all in kg.-cals.) :

			Diff.	
(I)	2268.6 ± 2.31	(II)	2165.5 ± 2.77	103.1
(III)	2188.6 ± 2.85	(IV)	2118.2 ± 2.34	70.4
Diff.	80.0		47.3	32.7

The difference between the constitutions of (III) and (IV) is the same as between 2 mols. of ethane and 2 mols. of ethylene. The difference between their molecular heats of combustion is 70.4 kg.-cals., which is in good agreement with that between the heats of combustion of 2 mols. of ethane and 2 mols. of ethylene, which, according to Thomsen, is 74.2 kg.-cals. The difference between the heats of combustion of (I) and (II), however, is 103.1 kg.-cals.; 2 : 6-diphenylthiopyrone (II) therefore contains less energy than that required by an exact conformity with formula (I). This deficit of 32.7 kg.-cals. is the "energy of aromatisation" of the pyronic nucleus. By considering the problem from another angle, it is seen that the difference between the heats of combustion of (I) and (III) is 80.0 kg.-cals. This difference is the heat of "combustion" of S to SO₂ within the molecule. The difference between the heats of combustion of (II) and (IV) is only 47.3 kg.-cals. This means that on oxidation of the sulphur atom in the thiopyrone (II) to the sulphone group in (IV), 32.7 kg.-cals. of the 80.0 kg.-cals. gained by the oxidation are used up in destroying the cyclic conjugation in (II) which is no longer present in (IV).

SUMMARY.

The dipole moments of 2 : 6-diphenylthiopyrone, 2 : 6-diphenylthiopyran-4-one, and their dioxides have been measured, and the results discussed in relation to their heats of combustion. The conclusions previously reached by one of the authors (Arndt) regarding the constitution of these compounds have been confirmed.

The authors thank the Royal Society for a grant. One of the authors (F. A.) wishes to express his deep gratitude to Professor R. Robinson, F.R.S., for his kind hospitality.

QUEEN MARY COLLEGE, UNIVERSITY OF LONDON.
DYSON PERRINS LABORATORY, OXFORD.

[Received, February 27th, 1935.]