The Dipole Moments of Some Sesquifulvalene Quinones and Related Compounds

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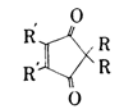
(Received August 7, 1964)

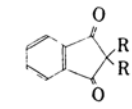
Although it is considered probable, from theoretical considerations, that sesquifulvalene is a highly polar molecule due to a charge transfer from the electron-donating seven-membered ring towards the electron-accepting five-membered ring, experimental evidence for this conclusion has not yet been provided because sesquifulvalene is not stable and easily polymerizes.[1-4] Recently Kitahara et al.[5] have synthesized some stable quinone derivatives of sesquifulvalene—sesquifulvalene-1, 4-quinone (VII) and 2, 3-benzosesquifulvalene-1, 4-quinone (VIII). Each of these quinones has two electron-withdrawing carbonyl groups in the five-membered ring, so that a considerable amount of charge transfer should be expected between the two rings. Accordingly, their dipole moments should provide some information with respect to this charge transfer. In order to obtain more detailed information, however, an investigation of the dipole moments of some diones related to the above quinones must also be undertaken. Therefore, besides those for the sesquifulvalene quinones, the dipole moments were measured for several compounds not having a heptafulvene structure—cyclopentene-3, 5-dione, indane-1, 3-dione, and their halogeno and tropyl derivatives.

Experimental

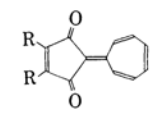
The following samples were used: cyclopentene-3, 5-dione (I), m. p. 37—38°C,[6] 4, 4-ditropylcyclopentene-3, 5-dione (II), m. p. 121—122°C,[5] 1, 2-dichlorocyclopentene-3, 5-dione (III), m. p. 163°C,[7] 1, 2-dichloro-4,4-ditropylcyclopentene-3,5-dione (IV), m. p. 103—104°C[5], indane-1, 3-dione (V), m. p. 132—133°C,[8] 2, 2-ditropylindane-1, 3-dione (VI), m. p. 167.5—168°C[5] [reported m. p. 173—174°C[9]]), sesquifulvalene-1, 4-quinone (VII), m. p. 179—180°C,[5] 2, 3-benzosesquifulvalene-1, 4-quinone (VIII), m. p. 244—245°C,[5] and 2, 3-dichlorosesquifulvalene-1, 4-quinone (IX), m. p. 263°C (decomp.).[5]



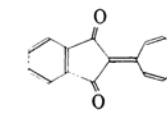
I R=R′=H
II R=C_7H_7; R′=H
III R=H; R′=Cl
IV R=C_7H_7; R′=Cl



V R=H
VI R=C_7H_7



VII R=H
IX R=Cl



VIII

The dipole moments of these substances were measured in benzene at 25°C using a high-inpedance a. c. bridge method described previously.[10] The benzene was purified as before.[10] The dipole moments were calculated using the method and equation of Halverstadt and Kumler:[11]

$$P_{2\infty}=(\varepsilon_1-1)/(\varepsilon_1+2)\cdot(v_1+\beta)M_2 + 3\alpha v_1 M_2/(\varepsilon_1+2)^2$$

$$\mu=0.012812\sqrt{(P_2-R_D)T}$$

The plots of ε_{12} versus w_2 and v_{12} versus w_2 were straight lines within the limits of experimental error. The values of ε_1 and v_1 were obtained by the method of least squares. The molar refractions, R_D, were calculated from the bond refraction data.[12] For 1, 2-dichlorocyclopentene-3, 5-dione and 1, 2-dichloro-4, 4-ditropylcyclopentene-3, 5-dione, however, because of their low dipole moments, the refractive indices at the D-line were measured using a Purflich refractometer, and the molar refractions were obtained from the following equa-

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TABLE I. THE DIPOLE MOMENT DATA IN BENZENE AT 25°C

(I) Sesquifulvalene-1, 4-quinone

$10^4 w_2$	ε_{12}	v_{12}		
0.8815	2.2731	1.14474	$\varepsilon_1=2.2732$	$\alpha=4.987$
2.8899	2.2748	1.14464	$v_1=1.14475$	$\beta=-0.331$
7.2037	2.2773	1.14448	$P_{2\infty}=217.42$	$R_D=51.27$ calcd.
12.0515	2.2791	1.14435	$\mu=2.85$ D.	
18.4768	2.2822	1.14415		

(II) 2, 3-Benzosesquifulvalene-1, 4-quinone

2.2029	2.2740	1.14475	$\varepsilon_1=2.2733$	$\alpha=3.213$
5.2757	2.2750	1.14462	$v_1=1.14483$	$\beta=-0.414$
10.7722	2.2767	1.14438	$P_{2\infty}=192.57$	$R_D=66.59$ calcd.
19.5782	2.2794	1.14400	$\mu=2.48$ D.	
27.7886	2.2823	1.14370		

(III) 2, 3-Dichlorosesquifulvalene-1, 4-quinone

3.7649	2.2771	1.14444	$\varepsilon_1=2.2730$	$\alpha=10.685$
5.0349	2.2782	1.14431	$v_1=1.14463$	$\beta=-0.545$
6.8195	2.2804	1.14430	$P_{2\infty}=553.56$	$R_D=60.93$ calcd.
9.2968	2.2829	1.14410	$\mu=4.91$ D.	

(IV) Cyclopentene-3, 5-dione

2.1889	2.2734	1.14560	$\varepsilon_1=2.2728$	$\alpha=3.623$
5.7821	2.2751	1.14543	$v_1=1.14563$	$\beta=-0.317$
12.6409	2.2772	1.14519	$P_{2\infty}=89.25$	$R_D=22.70$ calcd.
21.0662	2.2806	1.14494	$\mu=1.80$ D.	
34.2452	2.2851	1.14454		

(V) 4, 4-Ditropylcyclopentene-3, 5-dione

0.2586	2.2725	1.14511	$\varepsilon_1=2.2726$	$\alpha=1.320$
1.8458	2.2730	1.14504	$v_1=1.14510$	$\beta=-0.286$
10.0227	2.2741	1.14478	$P_{2\infty}=139.35$	$R_D=80.79$ calcd.
16.4297	2.2748	1.14463	$\mu=1.69$ D.	
25.0302	2.2759	1.14439		

(VI) Indane-1, 3-dione

3.5277	2.2745	1.14468	$\varepsilon_1=2.2728$	$\alpha=5.506$
6.7824	2.2766	1.14460	$v_1=1.14479$	$\beta=-0.310$
12.5974	2.2800	1.14439	$P_{2\infty}=187.72$	$R_D=35.43$ calcd.
23.1803	2.2854	1.14408	$\mu=2.73$ D.	

(VII) 2, 2-Ditropylindane-1, 3-dione

0.3809	2.2727	1.14524	$\varepsilon_1=2.2728$	$\alpha=2.723$
2.4533	2.2736	1.14519	$v_1=1.14525$	$\beta=-0.300$
8.7616	2.2752	1.14500	$P_{2\infty}=249.44$	$R_D=96.11$ calcd.
17.0778	2.2775	1.14470	$\mu=2.74$ D.	
24.5799	2.2794	1.14454		

(VIII) 1, 2-Dichlorocyclopentene-3, 5-dione

$10^3 w_2$	ε_{12}	v_{12}	n^2_{12}		
1.1253	2.2729	1.14405	—	$\varepsilon_1=2.2726$	$\alpha=0.470$
3.5924	2.2745	1.14278	2.24484	$v_1=1.14463$	$\beta=-0.516$
6.0176	2.2756	1.14154	2.24517	$n_1^2=2.24448$	
8.3489	2.2763	1.14032	2.24535	$\gamma=0.107$	
				$P_{2\infty}=45.48$	
				$R_D=33.77$ (32.37 calcd.)	
				$\mu=0.76$ D. (0.80 D.)*	

(IX) 1, 2-Dichloro-4, 4-ditropylcyclopentene-3, 5-dione

1.4302	2.2734	1.14422	—		
2.4639	—	1.14384	—	$\varepsilon_1=2.2730$	$\alpha=0.427$
2.6318	2.2744		2.24496	$v_1=1.14479$	$\beta=-0.394$
3.5235	2.2747	1.14339	—		
4.8600	2.2749	1.14287	2.24541	$n_1^2=2.24444$	
6.4273	2.2756	1.14226	2.24571	$\gamma=0.198$	
10.1467	2.2774	1.14079	—	$P_{2\infty}=107.68$	
				$R_D=91.34$ (90.46 calcd.)	
				$\mu=0.88$ D. (0.92 D.)*	

* The moment values in parentheses were obtained using the R_D value calculated from bond refraction data.

tion, which is similar to Halverstadt and Kumler's:

$$R_D=(n_1^2-1)/(n_1^2+2)\cdot(v_1+\beta)M_2 + 3\gamma v_1 M_2/(n_1^2+2)^2$$

Where γ is the slope of n_1^2 against w_2. The values of n_1^2 and γ were also obtained by the method of least squares. The molar refractions thus obtained were in substantial agreement with the calculated values. The data are shown in Table I. The dipole moments of the diones and sesquifulvalene quinones are listed in Tables II and III respectively.

TABLE II. THE DIPOLE MOMENTS OF CYCLOPENTENE DIONE, INDANE DIONE AND SOME DERIVATIVES

Compound	μ, D.
Cyclopentene-3, 5-dione	1.80
4, 4-Ditropylcyclopentene-3, 5-dione	1.69
1, 2-Dichlorocyclopentene-3, 5-dione	0.76
1, 2-Dichloro-4, 4-ditropylcyclopentene-3, 5-dione	0.88
Indane-1, 3-dione	2.73
2, 2-Ditropylindane-1, 3-dione	2.74

TABLE III. THE DIPOLE MOMENTS OF SESQUIFULVALENE QUINONE AND ITS DERIVATIVES

Compound	μ, D.	$\Delta\mu$, D.
Sesquifulvalene-1, 4-quinone	2.85	4.27
2, 3-Benzosesquifulvalene-1, 4-quinone	2.48	3.90
2, 3-Dichlorosesquifulvalene-1, 4-quinone	4.91	

Results and Discussion

Cyclopentene- and Indane-diones.—The fact that the dipole moment of 1, 2-dichlorocyclopentene-3, 5-diones is ca. 1 D. lower than that of unsubstituted cyclopentene-3, 5-dione evidently indicates that the moment of cyclopentene-3, 5-dione is directed towards the methylenic carbon from the center of the ring, the same direction as the carbonyl resultant moment.

In the case of cyclopentene-3, 5-dione, the substitution of two tropyl groups on the methylenic carbon results in a decrease of ca. 0.1 D. (1.69 D. compared with 1.80 D.), whereas with its dichloro derivatives an increase of almost the same value is revealed (0.88 D. compared with 0.76 D.). This indicates that the tropyl resultant moment is in the same direction as the C–Cl resultant and that these two moments are in the direction opposite to that of the C=O resultant; the moment of 1, 2-dichlorocyclopentene-3, 5-dione is, therefore, directed towards the C–Cl resultant. The moment of the tropyl group, therefore, seems to be ca. 0.1 D. larger than the C–H moment when the positive pole of the C–H moment is assumed to lie on the hydrogen atom. On the other hand, in the case of indane-1, 3-dione there is scarcely any change in the moment for a similar substitution of the tropyl groups (2.74 D. compared with 2.73 D.).

If one assumes the five-membered ring to be a regular pentagon, the two C=O groups make an angle of 144°. Using the bond moments $\mu_{C-H}=0$ and $\mu_{C=O}=2.3$ D.,[13] the moments of both cyclopentene-3, 5-dione and indane-1, 3-dione are calculated to be 1.4 D. The observed moments are both larger than those calculated, the difference being 0.4 D. with the former molecule and 1.3 D. with the latter. Such an increase in the moment, called the mesomeric moment, may be attributed to the charge transfer brought about through the resonance interaction from the ethylene or benzene group to the C=O groups, such as:

These values are very close to the incremental moments in going from maleic anhydride (3.91 D.[14]) to succinic anhydride (4.2 D.[15]) and from the latter to phthalic anhydride (5.27 D.[15]).

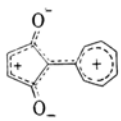
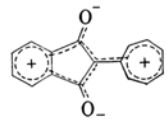
Sesquifulvalene Quinone.—If a change transfer does not occur between the five- and seven-membered rings, one would expect the dipole moments of sesquifulvalene-1, 4-quinone and its benzo derivative to be close to those of the corresponding diones which have been dealt with above. The experimental results for benzosesquifulvalene quinone seem nearly to bear this out, for it has a moment of 2.48 D. compared to the moment of 2.73 D. of indane-1,3-dione. On the contrary, the dipole moment of sesquifulvalene quinone is very high compared with that of cyclopentene dione, the difference in the moment being ca. 1 D. Thus these facts strongly suggest the possibility of a charge transfer interaction between the two rings present in these quinones. Regarding the direction of such a transfer, there are two possibilities to be considered, but one of them, transfer at the charge towards the seven-membered ring, is evidently in contradiction with the experimental data, as can be seen from a comparison of the moment of benzosesquifulvalene quinone with that of the corresponding indane dione. On the other hand, assuming that the transfer is oppositely

13) C. P. Symth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York (1955), p. 245.
14) L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Cambridge, Mass. (1948).
15) M. G. A. Rau and N. Anantanarayanan, *Proc. Indian Acad. Sci.*, A5, 185 (1937).

directed towards the five-membered ring and that the moments due to it are 4.7 and 5.2 D. respectively, values which are very large compared with those of the diones, then the observed relationship between sesquifulvalene quinones and the corresponding diones may be satisfactorily explained. Accordingly, the decrease in the moment of sesquifulvalene quinone upon the addition of a fused benzene ring may be understood as being due to the increase in the moment opposed to the charge transfer from the seven-membered ring. If the above reasoning is correct, one would expect a very large moment for the 2, 3-dichloro disubstituted derivative of sesquifulvalene quinone because the C–Cl resultant takes the same direction as the moment of sesquifulvalene quinone. Theoretical calculation predicts a moment of 4.95 D. for such a compound, using the bond moment $\mu_{C-Cl}=1.3$ D. deduced from the moment of *o*-dichlorobenzene (2.26 D.).[14] In fact, a value of 4.91 D. was observed for this quinone, a value in good agreement with the predicted one.

Thus one arrives at the conclusion that a remarkably large amount of charge transfer takes place from the seven-membered ring towards the five-membered ring in these sesquifulvalene quinones and that, consequently, their dipole moments are as a whole in the same direction as the charge transfer, and opposite to the C=O resultant.

By making the reasonable assumption that the five-membered rings of these quinones have regular pentagonal structures, as in cyclopentene dione and indane dione, the C=O resultant is calculated to have a value of 1.4 D., as before. Accordingly, the increase from this value, $\Delta\mu=\mu_{total}-2\mu_{C=O}$, is calculated to be 4.3 D. for sesquifulvalene quinone and 3.9 D. for its benzo derivative by subtracting vectorially the C–O resultant from each observed value; surprisingly, they are both very large and directed from the seven-membered ring towards the five-membered ring, the former being 1.1 times higher than the latter. These incremental moments may be ascribed to the contribution of such polar structures as:

When the inductive effects due to the C=O groups are disregarded, it follows that:

$$\Delta\mu=\mu_{total}-2\mu_{C=O}=\mu^{\pi}{}_{total}-2\mu^{\pi}{}_{C=O}$$

Even though various values, ranging from 1.5 D. to 0.3 D.,[1] have been estimated for the π-moment of a C=O group ($\mu^{\pi}{}_{C=O}$), it can only be said that the π-moment of sesquifulvalene-1, 4-quinone should be greater than that of benzosesquifulvalene-1, 4-quinone.

The charge transfer moment towards the five-membered ring may be obtained as follows. Taking the moments opposed to it as equal to 0.4 D. and 1.3 D., which have been found in the dione compounds, then the required transfer moments turn out to be 4.7 D. for sesquifulvalene quinone and 5.2 D. for its benzo derivative, the latter value being 1.1 times higher than the former. Although the above assumption regarding the magnitudes of the opposite moments is open to question, it seems very likely that the charge transfer from the seven-membered ring would be larger in benzosesquifulvalene quinone. The greatest part of these transfer moments may, of course, be considered to be due to the migration to the C=O groups, as may be seen from the contribution of the various polar structures. The charge migration in these sesquifulvalene quinones are also shown by the molecular orbital calculations. The electronic structures and the spectral data of these compounds will be discussed in detail later.

Summary

The dipole moments of some quinone derivative of sesquifulvalene, the corresponding dione compounds and their several derivatives have been measured in benzene at 25°C. The moments of cyclopentene-3, 5-dione and indane-1, 3-dione are in the same direction as the carbonyl resultant, the mesomeric moments being 0.4 D. and 1.3 D. respectively. On the other hand, the direction of the moments of sesquifulvalene-1, 4-quinone and its 2, 3-benzo derivative is just reversed because of a large transfer from the seven-membered ring towards the five-membered ring, presumably towards the carbonyl groups. The incremental moments, the difference between the observed and the carbonyl resultant, in these quinones are 4.2 and 3.9 D. respectively, while the moments due to the transfer from the seven-membered ring are 4.7 and 5.2 D., suggesting that such a charge transfer is greater in benzosesquifulvalene quinone.

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