The Dipole Moments and Molecular Structures of Croconic Acid and Dimethyl Croconate

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One of the present authors (K. Y.) and his co-workers have carried out extensive studies on the chemical properties of croconic acid and determined its structure to be cyclopentene-1-diol-1,2-trione-3,4,5[1]. They have measured the dipole moments of croconic acid and dimethyl croconate. Comparing the observed moments with those calculated by the method of molecular orbitals, they have undertaken to determine the electronic structures of these molecules as well as the geometrical arrangements of hydroxyl and methoxyl groups.

Experimental

Croconic acid and dimethyl croconate were synthesized and purified by one of them (K. Y.)[1]. Since these compounds were hygroscopic and the latter compound was readily hydrolyzed and gave the former, solvents were dried carefully. The dielectric constants and densities were measured of the solutions in dioxane or benzene. Because of the small solubilities, the measurements could not be extended to solutions of concentrations above 0.1 weight per cent. Therefore, it was difficult to determine the dipole moment very accurately.

The apparatus and the method of measurements were the same as used in our earlier works[2] except that a silvered cell of Sayce-Briscoe type[3] was used for the benzene solutions of dimethyl croconate. The Halverstadt-Kumler's method was employed. The dependence of the dielectric constants of the solutions of croconic acid in dioxane upon concentration was abnormal, the value of $\Delta\varepsilon/w$ increasing sharply with the decrease in concentrations. This fact suggests association or dissociation taking place. The results are shown in Tables I and II, where the same notations are used as in the previous reports[2].

TABLE I

DIELECTRIC CONSTANT AND DENSITY INCREMENTS OF SOLUTIONS OF CROCONIC ACID AND DIMETHYL CROCONATE

	Temp.	$w\times10^6$	$\Delta\varepsilon\times10^4$	$\Delta d\times10^5$
Croconic acid	25°C	80	68	—
in dioxane		233	156	—
		527	273	28
		1233	454	101
	35°C	140	91	0
		269	151	0
		507	220	0.3
		761	254	1.3
		937	264	2.8
Dimethyl croconate	30°C	306	53	—
in benzene		448	92	1.7
		645	134	—
		926	182	3.5
		1271	273	5.1

Discussion

The dipole moments of croconic acid and dimethyl croconate are high*. This indicates an appreciable contribution of polar structures to the ground state. The difference between the moments of the two compounds is as large as about 3~4 D. Since the group moment of C—OH is nearly the same as that of C—OCH_3 in its magnitude and also in its direction, the moments of the two compounds should be of the same order, unless an appreciable difference exists between the electronic and/or geometrical structures of the two compounds.

In calculating the moments of these compounds, one must take into account rotations about C—O single bonds. The moments were calculated for four conceivable configurations shown in Fig. 1. In the case of planar configurations, A and B, in which two OH or two OCH_3 groups lie in the ring plane, the two lone pairs belonging to the oxygen atoms conjugate with the rest of the molecule, so that twelve π-electrons are distributed

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1) K. Yamada, N. Mizuno and Y. Hirata, This Bulletin, **31**, 543 (1958).

* Accordingly, the structures having small moments, such as II or III in our previous report,[1] are not conceivable.

2) Y. Kurita, T. Nozoe and M. Kubo, ibid., **26**, 242 (1953).

3) M. Kobayashi, Y. Kurita and M. Kubo, *Chemistry and Chemical Industry* (*Kagaku to Kogyo*), **10**, 138 (1957).

TABLE II

MOLECULAR POLARIZATION AND DIPOLE MOMENTS

Compounds	Solvent	Temp.	ε_1	d_1 (g./cc.)	α	β (g./cc.)	$P_{2\infty}$ (cc.)	P_{A+E} (cc.)	μ(D)
Croconic acid	dioxane	25°C	2.2084	1.02755	80	0.86	1880	31	9.5 ±0.5
		35°C	2.1888	1.01565	76	0.00	1817	31	9.3 ±0.3
Dimethyl croconate	benzene	30°C	2.2625	0.86695	21	0.39	726	35	5.85±0.15

TABLE III

MOLECULAR ORBITAL ENERGIES AND WAVE FUNCTIONS[b)]

Symmetry[c)]	ω[a)]	c_1	c_2	c_3	c_4	c_5	c_6
				Planar configuration			
S	−3.8480	0.0929	0.1213	0.1677	0.1283	0.3426	0.5713
A	−3.4960	0	0	0.1060	0.1003	0.2290	0.6529
S	−3.1358	0.5255	0.4220	0.2901	0.3612	−0.0231	−0.2400
A	−2.7504	0	0	0.3230	0.6088	0.0275	−0.1556
S	−2.5196	0.6784	0.2493	−0.1656	−0.4507	−0.0292	0.0858
S	−0.7605	0.2686	−0.2355	−0.2795	0.3189	−0.4280	0.2703
S	0.1648	0.3738	−0.5723	−0.2172	0.1419	0.4074	−0.1819
A	0.2037	0	0	0.4995	−0.3206	0.3516	−0.1553
A	2.0427	0	0	0.3673	−0.1285	−0.5685	0.1595
S	2.0989	0.2076	−0.6017	0.4847	−0.1672	−0.1791	0.0498
				Perpendicular configuration			
S	−3.2515	0.4750	0.4204	0.3476	0.3927	0.1543	
A	−2.7913	0	0	0.3425	0.6120	0.0903	
S	−2.5447	0.7222	0.2782	−0.1568	−0.4070	−0.1015	
S	−1.2804	0.1606	−0.0817	−0.1659	0.3260	−0.5916	
S	0	0.4264	−0.6030	−0.3015	0.2132	0.3015	
A	0	0	0	0.4472	−0.3162	0.4472	
A	1.7913	0	0	0.4275	−0.1595	−0.5402	
S	2.0766	0.2126	−0.6129	0.4860	−0.1686	−0.1580	

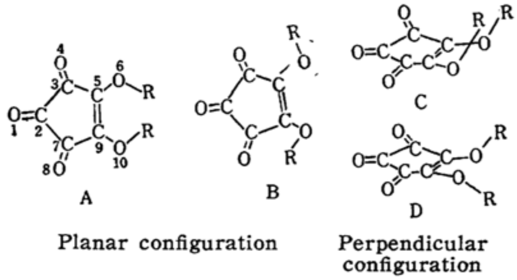
a) $\omega=(\alpha-E)/\beta$.

b) E: the energy of molecular orbital $\phi=\sum_r c_r\chi_r$. χ_r: atomic orbital of an r-th atom. As to numbering of atoms, see Fig. 1. Parameters used are as follows: Coulomb integrals are α, $\alpha+2\beta$, and $\alpha+3\beta$ for carbon atoms, carbonyl oxygen atoms and oxygen atoms of OH and OCH_3, respectively. Resonance integrals are β and $\sqrt{2}\beta$ for C-C and C-O bonds, respectively.

c) The suffixes S and A denote the symmetry properties of the molecular orbitals. For symmetric molecular orbitals, $c_7=c_3$, $c_8=c_4$, $c_9=c_5$ and $c_{10}=c_6$. For antisymmetric molecular orbitals, $c_7=-c_3$, $c_8=-c_4$, $c_9=-c_5$ and $c_{10}=-c_6$.

among ten atoms. On the other hand, for the perpendicular configurations, C and D, in which two OH or two OCH_3 groups lie in the plane perpendicular to the ring, the conjugation decreases to its minimum. Then, it can be treated as a system of eight π-electrons distributed among eight atoms.

It is difficult to calculate adequately the moment of a molecule conjugated to such an extent as in croconic acid or dimethyl croconate from the vector addition of relevant bond moments. It is generally accepted that the simple method of molecular orbitals, which neglects mutual re-



Planar configuration

Perpendicular configuration

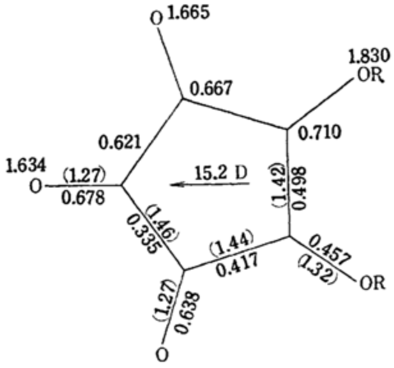
Fig. 1. Croconic acid (R=H) and dimethyl croconate ($R=CH_3$).

pulsion between electrons, always gives too high values for the theoretical moments. Orgel and his co-workers[4] presented an equation to calculate a total moment with due regard to mutual repulsion between electrons.

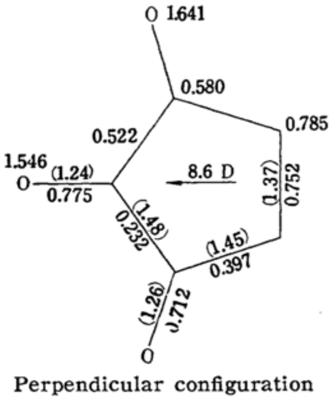
$$\vec{\mu}_T=\vec{\mu}_\sigma+\vec{\mu}_\pi/1.6 \qquad (1)$$

They applied this equation to eighteen conjugate heterocyclic compounds and obtained theoretical moments in agreement with the observed ones within 0.30 D in magnitudes and 10° in directions. Following their procedure, we calculated the dipole moments.

In Table III are shown the energies and the coefficients of atomic orbitals in molecular orbitals constructed from π-orbitals belonging to atoms participating in conjugation. Ten and eight atoms are involved in the planar and perpendicular configurations, respectively. In Fig. 2 are shown the corresponding molecular diagrams accommodated with twelve or eight π-electrons allotted to the molecular orbitals of low energies. The bond lengths were calculated from bond orders using the relation described in a preceding report[5]. In each diagram, the estimated μ_π is shown, which was obtained by assuming that the pentagon ring is approximately regular, that the carbon-oxygen bonds lie along the lines from the center of the ring to the respective carbon atoms, and that the bond distances are as given above. On the other hand, μ_σ was calculated with the assumption that the bond moments of OH and OCH_3 were equal to 1.5 D and 1.2 D, respectively, and that the valency angles ∠COH and $\angle COCH_3$ were 105° and 110°, respectively. The total moments calculated from equation 1 are shown in Table IV, together with the observed moments.



Planar configuration



Perpendicular configuration

Fig. 2. Molecular diagrams: π-electron densities, bond orders, bond lengths (in parentheses), and μ_π.

TABLE IV

DIPOLE MOMENTS (D)

Configuration		Croconic acid	Dimethyl croconate
Planar	A	8.4	8.8
	B	10.4	10.3
Perpendicular	C	6.7	6.5
	D	6.0	6.0
Observed		9∼10	5.7∼6.0

The moment of dimethyl croconate can adequately be explained by the perpendicular configurations. The planar configurations are unlikely in view of the steric hindrance acting between the methyl groups or between the methyl group and the carbonyl oxygen atom. The observed moment of croconic acid is in good agreement with those of the planar configurations. In these configurations, the conjugation within the molecule can attain its maximum possible extent. Moreover, a hydrogen bond can be formed between the OH group and carbonyl oxygen or between the OH groups. The hydrogen bond formation stabilizes the molecule and increases the trend of electron attraction of carbonyl oxygen.

The first excitation energy associated with π-electron was calculated as 0.925β, 1.280β and 0.813β* for the planar and perpendicular configurations and for a croconate ion $C_5O_5^{--}$, respectively. This energy level can be shown to be capable of accounting for the spectral features of

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[4] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

[5] Y. Kurita and M. Kubo, This Bulletin, **24**, 13 (1951).

* It was calculated with the assumption that croconate ion is planar and symmetrical and the Coulomb integral of oxygen atom is $\alpha + 2.4\ \beta$.

the acid and its dimethyl ester as well as the changes in their spectra with solvents[1].

Summary

The dipole moments of croconic acid and dimethyl croconate were measured in dioxane and benzene solutions, respectively, as 9∼10 D and 5.7∼6.0 D. The moments of these molecules were calculated theoretically for several conceivable configurations by the method of molecular orbitals. The results confirm the structure presumed from evidences in organic syntheses. The accumulation of π-electrons on carbonyl oxygen is chiefly responsible for the large dipole moments, the effect being stronger in the acid. The hydroxyl groups of croconic acid lie in the ring plane, whereas the methoxyl groups are out of the ring plane to minimize the steric hindrance.

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