The Calculation of the State Energies of *cis*- and *trans*-Terephthalaldehyde

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Terephthalaldehyde is a carbonyl derivative of benzaldehyde and its *cis*- and *trans*-forms in solution have been found by Maki¹⁾ by means of ESR experiments.

Since *cis*-terephthalaldehyde has the C_{2v} symmetry, its π-electronic state belongs to the A_1 or B_1 of the C_{2v} symmetry group. Electronic transitions of A_1 and B_1 types have transition moments parallel to the z and x axes respectively.

On the other, *trans*-terephthalaldehyde has the C_{2h} symmetry and its π-electronic state belongs to the irreducible representation, A_g or B_u, of the symmetry group. Electronic transitions from the A_g ground state to the A_g excited states are impossible, but transitions to the B_u excited state are possible. Their transition moments are localized in the molecular plane.

We calculated the state energies for the two isomers by the semiempirical SCF-MO-CI method. The calculated procedure was the same as that used in a previous paper,²⁾ in which the state energies of benzaldehyde were calculated. The molecular models of *cis*- and *trans*-terephthalaldehydes are shown in Fig. 1, in which the bond angle of C–C=O is assumed to be 120°.

Results and Discussion

The SCF-MOs and MO energies are listed in Table I. In large molecules multiply-excited configurations should make a negligibly small contribution to the lower excitation energies. Therefore, we take account of single excitations only in the present calculation. The configuration

TABLE I. SCF-MOs AND THEIR ENERGIES OF *cis*-TEREPHTHALADEHYDE (I) AND *trans*-TEREPHTHALALDEHYDE (II)

(I)	MO	Sym	$(\chi_1\pm\chi_{10}{}^*)$	$(\chi_2\pm\chi_9)$	$(\chi_3\pm\chi_6)$	$(\chi_4\pm\chi_5)$	$(\chi_7\pm\chi_8)$	ε_i, eV.
	1	b_2	0.23522	0.22994	0.39085	0.36480	0.32551	−16.1377
	2	a_2	−0.53149	−0.39424	−0.22251	−0.08270	0.07577	−15.1986
	3	b_2	−0.53837	−0.32042	0.14416	0.21913	0.19670	−14.5752
	4	b_2	−0.00759	0.00637	0.03124	−0.48815	0.51053	−12.4567
	5	a_2	0.27285	0.03923	−0.53202	−0.27160	0.25923	−12.3713
	6	b_2	0.28375	−0.33686	−0.42022	0.24236	0.26587	− 2.1367
	7	a_2	−0.06492	0.09752	0.02813	−0.53373	−0.44789	− 1.0182
	8	a_2	−0.36143	0.54141	0.02278	−0.07749	0.26405	− 0.4924
	9	b_2	0.27250	−0.48057	0.38587	−0.14792	−0.15500	0.6996
	10	a_2	0.09068	−0.20100	0.40760	−0.35849	0.39588	2.4959
(II)	MO	Sym	$(\chi_1\pm\chi_{10}{}^{**})$	$(\chi_2\pm\chi_9)$	$(\chi_3\pm\chi_6)$	$(\chi_4\pm\chi_7)$	$(\chi_5\pm\chi_8)$	ε_i, eV.
	1	a_u	0.23700	0.23089	0.39093	0.35030	0.33910	−16.1380
	2	b_g	−0.53195	−0.39376	−0.22194	−0.08932	0.06883	−15.2072
	3	a_u	−0.53803	−0.31909	0.14595	0.21053	0.20755	−14.5834
	4	b_g	−0.12466	−0.02692	0.22092	0.56903	0.33338	−12.4904
	5	b_g	0.24247	0.02981	−0.48449	−0.02269	0.45285	−12.3486
	6	a_u	0.28233	−0.33625	−0.41978	0.29191	0.21401	− 2.1527
	7	a_u	−0.02610	0.02992	0.02374	0.47582	−0.52102	− 0.9905
	8	b_g	−0.36664	0.55020	0.02765	−0.17113	0.18110	− 0.5149
	9	a_u	0.27196	−0.48054	0.38613	−0.14613	−0.15708	0.6953
	10	b_g	0.09091	−0.20152	0.40798	−0.37206	0.38243	0.4890

* Double signs ± mean $\chi_1+\chi_{10}$ for symmetry b_2 and $\chi_1-\chi_{10}$ for a_2.

** $\chi_1+\chi_{10}$ for symmetry a_u and $\chi_1-\chi_{10}$ for b_g.

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1) A. H. Maki, *J. Chem. Phys.*, **35**, 761 (1961).

2) K. Inuzuka and T. Yokota, This Bulletin, **38**, 1055 (1965).

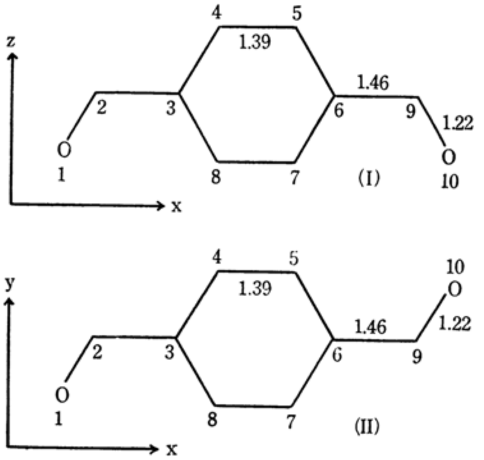

Fig. 1. Molecular models of *cis*- and *trans*-terephthalaldehydes (I and II).

mixing for *cis*-terephthalaldehyde leads to two 12th-order secular equations for the $^1A_1$ and $^3A_1$ states, and to two 13th-order secular equations for the $^1B_1$ and $^3B_1$ states. For *trans*-terephthalaldehyde, configuration mixing leads to two 12th-order secular equations for ^1A_g and ^3A_g states and to two 13th-order secular equations for ^1B_u and ^3B_u states. The state energies and wave functions are obtained from the solutions of these secular equations. The lower-lying state energies and oscillator strengths are listed in Table II.

TABLE II. CALCULATED ENERGY LEVELS OF TEREPHTHALALDEHYDE

	cis			*trans*			Obs. eV.
	State	*E*, eV.	*f*	State	*E*, eV.	*f*	
G	$^1A_1$	0		^1A_g	0		0
1	$^1A_1$	4.657	0.017	^1B_u	4.645	0.040	4.05
2	$^1B_1$	4.859	0.165	^1B_u	4.868	0.164	4.68
3	$^1B_1$	6.269	1.15	^1B_u	6.250	0.963	6.13
4	$^1A_1$	6.429	0.033	^1A_g	6.540	0	
5	$^1A_1$	6.823	0.704	^1B_u	6.736	0.962	
1	$^3B_1$	3.145		^3B_u	3.143		
2	$^3A_1$	3.845		^3A_g	3.856		
3	$^3B_1$	3.948		^3B_u	3.928		
4	$^3A_1$	4.029		^3B_u	4.042		

We observed terephthalaldehyde to have three $\pi-\pi^*$ absorption bands, at about 300, 260 and 200 mμ, in an *n*-hexane solution. The energy values corresponding to these absorption bands are also listed in Table II. The calculated values are in agreement with the observed values. From Table II we can not find any significant difference in state energies between the *cis*-isomer and the *trans*-isomer, but the 1st excited energy of the *trans*-isomer is lower than that of the *cis*-isomer. The values of the Coulomb integral are almost invariant over a great atomic distance. The change in the position of the carbonyl group from the *trans*-form to the *cis*-form does not have any appreciable effect on the molecular integral, because the distance between carbonyl groups is large. The similarity in electronic structure of *cis*- and *trans*-terephthalaldehydes is attributed to the above fact. The absorption spectrum of terephthalaldehyde resembles that of benzaldehyde. The spectrum of the former shifts to a longer wavelength side than that of the latter. The similarity in absorption spectra can be seen in the transition energies and oscillator strengths obtained for benzaldehyde[2,3] and for terephthalaldehyde. The charge densities and the free valences of both isomers for the ground and lower excited states are listed in Table III. These values of the excited states are calculated by assuming the same molecular structures as in the ground state. The charge densities of the position 4 of *cis*- and *trans*-terephthalaldehydes indicate a high reactivity to electrophilic reagents.

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TABLE III. CHARGE DENSITIES (q_i) AND FREE VALENCES (f_i) OF *cis*-TEREPHTHALALDEHYDE (I) AND *trans*-TEREPHTHALALDEHYDE (II) IN THE GROUND AND LOWER EXCITED STATES

			q_1	q_2	q_3	q_4	q_7	f_2	f_3	f_4	f_7
(I)	State										
	$^1A_1$	G	1.404	0.625	1.101	1.000	0.957	0.617	0.214	0.411	0.415
	$^1A_1$	1	1.431	0.707	1.036	0.951	0.875	0.605	0.360	0.710	0.711
	$^1B_1$	2	1.405	0.716	0.939	0.997	0.943	0.598	0.463	0.627	0.618
	$^1B_1$	3	1.381	0.684	0.989	1.019	0.926	0.677	0.339	0.759	0.733
(II)	State		q_1	q_2	q_3	q_4	q_7	f_2	f_3	f_4	f_7
	^1A_g	G	1.406	0.624	1.014	0.999	0.958	0.618	0.215	0.412	0.413
	^1B_u	1	1.420	0.705	0.991	0.969	0.915	0.601	0.407	0.677	0.674
	^1B_u	2	1.415	0.706	0.979	0.995	0.905	0.599	0.418	0.649	0.678
	^1B_u	3	1.372	0.676	0.978	0.960	1.014	0.680	0.347	0.768	0.707

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3) K. Inuzuka and T. Yokota, ibid., **37**, 1224 (1964).