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X-ray Structures and Dipole Moments of Tropones Annulated with Furan, Benzene, and Oxepin

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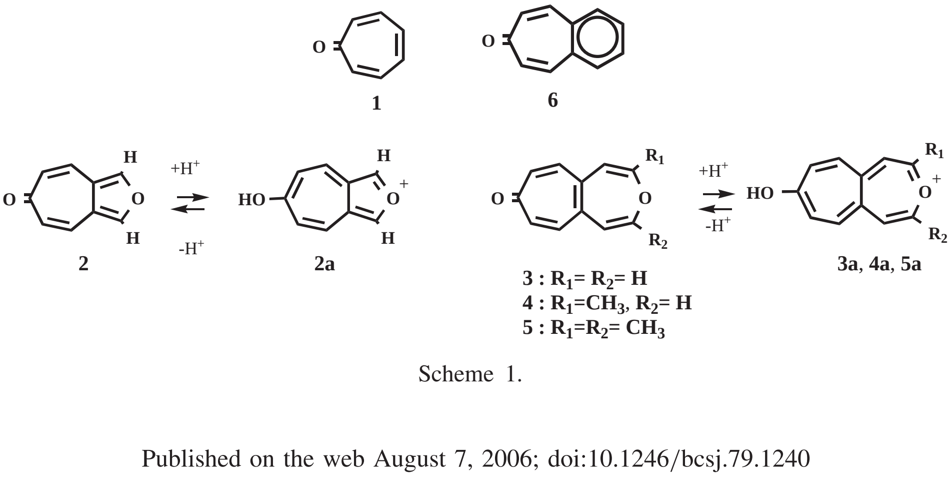
The precise X-ray structures of furo[3,4-*d*]tropone (**2**), 2,4-dimethyl-8*H*-3-oxaheptalen-8-one (**5**), and 4,5-benzotropone (**6**) were determined. Their tropone rings show definite bond alternation and nearly planar conformation, though slightly boat-shaped like polycyclic tropone. The ground-state dipole moments of **2**, **5**, and **6**, and also 8*H*-3-oxaheptalen-8-one (**3**) and 2-methyl-8*H*-3-oxaheptalen-8-one (**4**) were measured in benzene at 25 °C. Analyses of the ground-state dipole moments by means of ab initio calculations demonstrate that the polar structures of **2** and **6** having an annulated aromatic ring are based on the local dipoles of penta-1,4-dien-3-one and the induced dipole of the annulated ring, whereas those of **3** and **5** are based not only on the local dipoles but also on the partial intramolecular CT interaction from the olefinic oxepin ring to the pentadienone moiety. According to the McRae equation, the dipole moments of the two lowest excited states of **2**, **3**, **5**, and **6** were evaluated by using the frequency shifts of the absorption maxima in a number of polar and nonpolar solvents. They are all oriented in the same direction as that of the ground state, but are greater in magnitude.

The tropone (cycloheptatrienone) (**1**), a mother compound of seven-membered aromatics, has been a valuable building block for the synthesis of novel aromatics since the conversion methods of **1** into other seven-membered aromatics were established.[1] We have reported the syntheses of furo[3,4-*d*]tropone (**2**)[2] and the 8*H*-3-oxaheptalen-8-ones **3**–**5**.[3] Under the conditions of strong acid solutions, the annulated tropones **2**–**5** were protonated to give **2a**–**5a**, which are largely fully conjugated bicyclic systems.[2,3] X-ray structural analysis of **1** has shown a planar cycloheptatrienone with marked bond alternation[4] and analysis of the dipole moment in the ground state is adequately described by that of a polyolefinic ketone.[5] Here, we report the X-ray structures of the annulated tropones **2**, **5**, and **6** at low temperature (150 K) and the ground- and excited-state dipole moments of the annulated tropones **2**–**6**. Although the X-ray structures of many tropone derivatives[6] and a few annulated tropones[7] have been so far reported, we believe that the present study will give fundamental information for the annulated tropone system by the precise X-ray structures of the simple compounds **2**, **5**, and **6** (Scheme 1).



Scheme 1.

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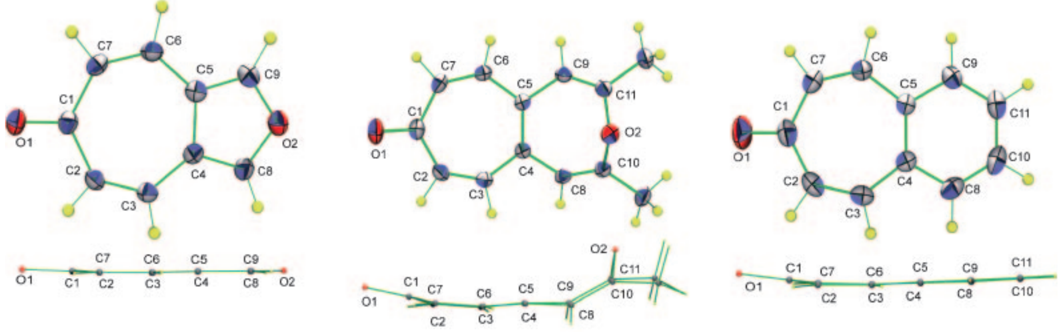


furo[3,4-*d*]tropone(**2**) 2,4-dimethyl-8*H*-3-oxaheptalen-8-one(**5**) 4,5-benzotropone(**6**)

Fig. 1. Molecular structures of the annulated tropones **2**, **5**, and **6**: upper, top view (ORTEP drawings with 50% probability thermal ellipsoids); below, side view (circles).

Results and Discussion

X-ray Structures of Furo[3,4-*d*]tropone (2), 2,4-Dimethyl-8*H*-3-oxaheptalen-8-one (5), and 4,5-Benzotropone (6). X-ray structural analyses were carried out for the annulated tropones **2**, **5**, and **6** at 150 K. The molecular drawings (top view and side view) are shown in Fig. 1 and the selected bond lengths, bond angles, and dihedral angles for the molecular planarity are summarized in Table 1. Even the structures of **2**, **5**, and **6**, including the hydrogen atoms, have approximate C_s symmetry within experimental error. In all compounds, the tropone rings show a definite bond alternation similar to other troponoids.[4,6,7] By the annulations of five-, seven-, and six-membered rings, the bond lengths and angles around the C4 and C5 atoms are remarkably but reasonably different from each other. It is especially noteworthy that the C4–C5 bond [1.445(4) Å] lengthened and the C4–C8 bond [1.361(4) Å] shortened for **2**, whereas the C4–C5 bond [1.387(2) Å] shortened and the C4–C8 bond [1.464(2) Å] lengthened for **5**. Their bond lengths [1.416(2) and 1.407(2) Å] for **6** correspond to aromatic bonds. Thus, it can be said that the observed bond lengths reflect the chemical formulae of **2**, **5**, and **6** shown in Scheme 1. It may be significant that the C=O bonds are lengthened in the order of **2** [1.242(3) Å], **5** [1.237(2) Å], and **6** [1.232(2) Å], although the values are in the range of the observed ones in the related compounds.[4,6,7] On the other hand, all tropone rings are nearly planar, although they are deformed into a slightly boat-shaped conformation. The boat conformation becomes deeper in the order **2**, **6**, and **5** due to the peri-interaction between H(C3) and H(C8), and H(C6) and H(C9). The oxepin ring of **5** takes a boat form and the C10–O2–C11 plane intersects the bottom plane (C2, C3, C6, and C7) of the tropone ring at 86.36(6)°, and two CH_3–C bonds of the oxepin ring of **5** are almost parallel to the bottom plane of the tropone ring [the dihedral angle is 3.96(8)°].

The Ground-State Dipole Moments of Furo[3,4-*d*]tropone (2), 8*H*-3-Oxaheptalen-8-one (3), Its 2-Methyl and 2,4-Dimethyl Derivatives 4 and 5, and 4,5-Benzotropone (6). The ground-state dipole moments of the annulated tropones **2**–**6** and 2,7-dimethyloxepin were measured at 25 °C in benzene solutions. The dipole moments of the molecules were determined from the equation in Debye unit: $\mu = 0.01281[(P_{2\infty} - R_{\mathrm{MD}})T]^{1/2}$ at the temperature T, in which $P_{2\infty}$ and R_{MD} mean the total polarization of the solute at infin-

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for **2**, **5**, and **6** with Their Esd's in Parentheses[a)]

		Bond lengths		
Bonds	Bonds[b)]	**2**	**5**	**6**
O1–C1		1.242(3)	1.237(2)	1.232(2)
C1–C2	C1–C7	1.468(4)	1.453(2)	1.458(2)
C2–C3	C6–C7	1.347(4)	1.349(2)	1.343(2)
C3–C4	C5–C6	1.439(4)	1.447(2)	1.450(2)
C4–C5		1.445(4)	1.387(2)	1.416(2)
C4–C8	C5–C9	1.361(4)	1.464(2)	1.407(2)
O2–C8	O2–C9	1.358(3)		
O2–C10	O2–C11		1.400(2)	
C8–C10	C9–C11		1.332(2)	1.377(2)
C10–C11				1.386(2)
		Bond angles		
Angles	Angles[b)]	**2**	**5**	**6**
O1–C1–C2	O1–C1–C7	117.3(2)	118.9(1)	119.6(1)
C2–C1–C7		125.5(2)	120.7(1)	122.2(1)
C1–C2–C3	C1–C7–C6	130.6(2)	130.2(1)	130.5(1)
C2–C3–C4	C5–C6–C7	128.3(2)	133.4(1)	132.5(1)
C3–C4–C5	C4–C5–C6	128.4(2)	124.9(1)	125.6(1)
C5–C4–C8	C4–C5–C9	105.7(2)	121.7(1)	118.3(1)
C3–C4–C8	C6–C5–C9	125.9(2)	113.2(1)	116.1(1)
O2–C8–C4	O2–C9–C5	110.0(2)		
O2–C10–C8	O2–C11–C9		120.3(1)	
C4–C8–C10	C5–C9–C11		127.5(1)	122.0(1)
C8–C10–C11	C9–C11–C10			119.7(1)
C8–O2–C9		106.6(2)		
C10–O2–C11			110.9(1)	
		Dihedral angles		
Two planes		**2**	**5**	**6**
C1C2C7/C2C3C6C7		1.83(10)	10.32(6)	6.84(6)
C2C3C6C7/C3C4C5C6		1.76(17)	7.49(8)	2.91(9)
C3C4C5C6/C4C8C9C5		1.16(17)	4.83(8)	0.90(7)
C4C8C9C5/C8C10C11C9			28.0(8)	1.28(9)
C4C5C8C9/C8O2C9		0.24(12)		
C8C10C11C9/C10O2C11			55.49(6)	
C2C3C6C7/C8O2C9			86.34(6)	

a) Bond lengths and angles are averaged by assuming C_s symmetry. b) The equivalent bonds and angles.

Table 2. Weight Fractions (ω_2) vs Dielectric Constants (ε_{12}) and Specific Volumes (v_{12}) of Annulated Tropones **2**–**6**, and 2,7-Dimethyloxepin

Compound	$\omega_2 \times 10^4$	ε_{12}	v_{12}/cm^3 g^{-1}	Compound	$\omega_2 \times 10^4$	ε_{12}	v_{12}/cm^3 g^{-1}
2	0.4087	2.2782	1.14443	**5**	2.3770	2.2770	1.14447
	0.7527	2.2813	1.14430		6.2843	2.2843	1.14431
	1.1831	2.2862	1.14410		12.8152	2.2962	1.14409
	1.7445	2.2933	1.14381		20.9881	2.3121	1.14374
3	2.3025	2.2759	1.14439	**6**	4.5349	2.2799	1.14438
	3.1333	2.2770	1.14438		8.2185	2.2855	1.14416
	5.5104	2.2809	1.14429		13.480	2.2938	1.14397
	5.6744	2.2812	1.14422		18.343	2.3016	1.14374
	11.2179	2.2819	1.14396		25.081	2.3121	1.14336
4	0.31086	2.2781	1.14443	2,7-Dimethyl-oxepin	1.0378	2.2748	1.14413
	0.69714	2.2858	1.14428		2.7712	2.2787	1.14350
	1.0948	2.2950	1.14413		5.2876	2.2842	1.14244
	2.1143	2.3112	1.14368		8.3723	2.2909	1.14115
					12.0496	2.2979	1.13973

Table 3. Empirical Parameters (ε_1, v_1, α, and β), Total Polarization ($P_{2\infty}$) of the Solutes, and Molar Refractions (R_{MD}) for the Sodium *D* Lines of Annulated Tropones **2**–**6**, and 2,7-Dimethyloxepin

Compound	ε_1	v_1/cm^3 g^{-1}	α	β/cm^3 g^{-1}	$P_{2\infty}$/cm^3	R_{MD}/cm^3
2	2.2731	1.14464	11.396	−0.467	342.719	42.936
3	2.2724	1.14453	15.224	−0.498	526.241	48.434
4	2.2726	1.14457	18.222	−0.417	678.585	53.082
5	2.2724	1.14456	18.820	−0.387	754.068	57.73
6	2.2727	1.14459	15.721	−0.481	492.703	46.65
2,7-Dimethyloxepin	2.2729	1.14457	2.106	−0.404	75.339	41.094

ite dilution and the molar refraction, respectively. The molar refraction R_{MD} suffers from the contribution of bond refraction and atomic polarization, although that of atomic polarization is relatively small and its precise estimation is difficult. In this work, the R_{MD} are evaluated from the sum of the bond refractions. We determined the total polarization of the solute at infinite dilution using the method of Halverstadt and Kumler[8] based on the following equation:

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

in which M_2 is the molecular weight of solute and ε_1 and v_1 are the dielectric constant and specific volume of the solvent, benzene, respectively. The dielectric constants and specific volumes were observed for the solvent, benzene, and for dilute solutions with different weight fractions of the solute. The measured values of the dielectric constants, ε_{12}, and the specific volumes, v_{12}, of the solutions exhibit a linear dependence on the weight fraction, ω_2, of the solute, as given by the equations:

$$\varepsilon_{12} = \varepsilon_1 + \alpha\omega_2, \tag{2}$$

$$v_{12} = v_1 + \beta\omega_2, \tag{3}$$

in which the coefficients α and β were obtained by least-squares fitting of the above equations. The total polarizations of the solute at infinite dilution, $P_{2\infty}$, were calculated by the equation using the empirical data described above. Table 2 shows the weight fractions, ω_2, vs. dielectric constants, ε_{12}, and specific volumes, v_{12}, of **2**–**6** and 2,7-dimethyloxepin. The total polarization, $P_{2\infty}$, of the solutes and molar refractions, R_{MD}, for the sodium D line are shown in Table 3 along with the values, α, β, ε_1, and v_1.

The observed dipole moments are shown in Table 4 together with the reported value of furan. To assess the observed data, three different types of calculations (HF, MP2, and B3LYP) were performed with the 6-311G** basis set (hereafter we use the abbreviation, for example, B3LYP/6-311G** at the B3LYP calculation with using 6-311G** basis set). In the calculations of the annulated tropones **2**, **5**, and **6**, the molecular geometries used were the ones obtained by the X-ray analyses, the molecular coordinate is that where the bottom plane (C2, C3, C6, and C7) of the tropone ring is assigned to be the *xy* plane and the *xz* plane is taken to bisect the tropone ring through C1 and the center of the C4–C5 bond. The calculated dipole moments are shown in Table 4. Of these calculations, the MP2 method gave values in reasonable agreement with the observed values. We have no structure by X-ray analysis for 8*H*-3-oxaheptalen-8-one (**3**), so we carried out two types of calculations, MP2/6-311G**//B3LYP/6-311G** and HF/6-311G**//HF/6-311G**, which resulted in dipole moments of 4.410 D and 4.978 D, respectively: The latter value is near the observed value 4.8 D. The dipole moments of furan and 2,7-dimethyloxepin were calculated also with MP2/6-311G**//MP2/6-311G**.

Qualitative comparison of the dipole moments of the annulated tropones in terms of the observed dipole moments for the nearly planar molecules **2** and **6** and the calculated dipole moment along the *x* axis, μ_x, of the bending molecule **5** displays

Table 4. Observed and Calculated Dipole Moments (D) of Furan, 2,7-Dimethyloxepin, and Annulated Tropones **2–6**

	Furan	**2**	**6**	2,7-Dimethyl-oxepin	**3**	**4**	**5**
Observed/D[a]	0.71[e]	3.83	4.67 4.70[f] 4.88[g]	1.29	4.84	5.43	5.84
Calculated/D[b] (μ_x), (μ_y), (μ_z)[c] [level][d]	0.528 $(\mu_x = -0.528)$ $(\mu_y = 0.000)$ $(\mu_z = 0.000)$ [MP2/6-311G** //MP2/6-311G**]	4.630 $(\mu_x = 4.628)$ $(\mu_y = -0.043)$ $(\mu_z = -0.139)$ [HF/6-311G**]	4.665 $(\mu_x = 4.656)$ $(\mu_y = 0.007)$ $(\mu_z = -0.280)$ [MP2/6-311G**]	1.374 $(\mu_x = 0.833)$ $(\mu_y = -0.000)$ $(\mu_z = -1.092)$ [MP2/6-311G** //MP2/6-311G**]	4.978 $(\mu_x = 4.853)$ $(\mu_y = 0.000)$ $(\mu_z = -1.109)$ [HF/6-311G** //HF/6-311G**]		7.260 $(\mu_x = 6.873)$ $(\mu_y = -0.001)$ $(\mu_z = -2.340)$ [HF/6-311G**]
		4.369 $(\mu_x = 4.367)$ $(\mu_y = -0.040)$ $(\mu_z = -0.122)$ [B3LYP/6-311G**]			4.410 $(\mu_x = 4.309)$ $(\mu_y = 0.000)$ $(\mu_z = -0.940)$ [MP2/6-311G** //B3LYP/6-311G**]		6.854 $(\mu_x = 6.530)$ $(\mu_y = -0.002)$ $(\mu_z = -2.080)$ [B3LYP/6-311G**]
		3.844 $(\mu_x = 3.842)$ $(\mu_y = -0.038)$ $(\mu_z = -0.115)$ [MP2/6-311G**]					6.111 $(\mu_x = 5.776)$ $(\mu_y = -0.004)$ $(\mu_z = -1.997)$ [MP2/6-311G**]

a) Observed in benzene at 25 °C. b) Calculated on the basis of X-ray structures for **2**, **6**, and **5**, and no calculation for **4**. c) *xy* Plane is assigned to be that of C2, C3, C6, and C7 plane of tropone, and *xz* plane bisects the tropone ring through C1 and the center of C4–C5 bond. d) Levels in the calculations, [level A//level B] means the level A calculations using the level B optimized structures. e) A. L. McClellan, *Tables of Experimental Dipole Moments*, W. H. Freeman and Company, San Francisco and London, **1963**, p. 101. f) T. Gaumann, R. W. Schmidt, E. Heilbronner, *Helv. Chim. Acta* **1956**, *230*, 1985. g) T. Shimozawa, S. Kumakura, M. Hoshino, S. Ebine, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 565.

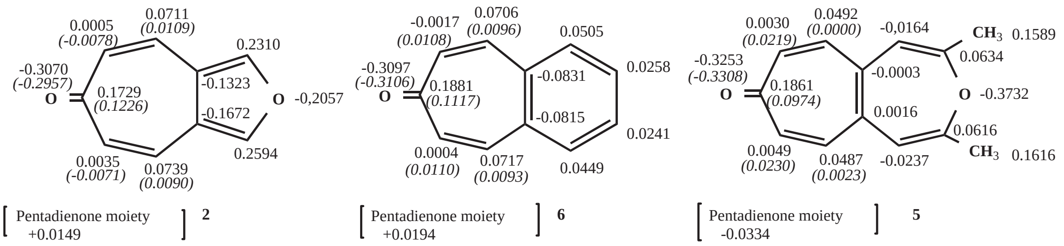


Fig. 2. Net electronic charges (positive, cationic) of the annulated tropones **2**, **6**, and **5** calculated at the MP2/6-311G** level, based on their X-ray structures. Hydrogen net charge is added to the carbon charge. Values in parentheses (*Italic*) are valence π net electronic charges, for which the contributions from the polarization functions are also included.

that the dipole moment increases in the order: **2** (3.83 D) < **6** (4.67 D) < **5** ($\mu_x = 5.78$ D; MP2/6-311G** calculation). Considering that the annulated tropones consist of the penta-1,4-dien-3-one moiety and the annulated ring, this order is in accord with the order of the moment of their annulated ring arranged in such a way that they are each parts of the condensed systems: furan (-0.53 D) < benzene (0 D) < 2,7-dimethyloxepin ($\mu_x = 0.83$ D).

X-ray analysis of 2,4-dimethyl-8*H*-3-oxaheptalen-8-one (**5**) exhibits that two CH_3–C bonds of **5** are oriented nearly parallel to the *xy* plane and the bond moment vectors are directed so as to increase the dipole moment of 8*H*-3-oxaheptalen-8-one. Similar spatial orientation could be assumed for the methyl group of the 2-methyl derivative **4**. These findings explain the successive increases in the dipole moments in the order; **3** < **4** < **5**.

Figure 2 shows the net electronic charges (positive, cationic) calculated with MP2/6-311G**, using the geometries determined by X-ray structural analyses. Regardless of the annulated ring, the penta-1,4-dien-3-one parts of **2** and **6** exhibit a very similar distribution of net electronic charges, in which marked charges are held by cationic carbonyl carbon and by anionic carbonyl oxygen. The sum of the net electronic charges on the pentadienone moiety is slightly positive for **2** and **6** (0.0149 and 0.0194, respectively) and negative for **5** (-0.0334). The corresponding charge of 8*H*-3-oxaheptalen-8-one (**3**), for which we have no molecular structure from the X-ray analysis and the charge was calculated using one from geometry optimization, leads to similar results [-0.0314 (MP2/6-311G**//B3LYP/6-311G**), -0.0106 (HF/6-311G**//HF/6-311G**)].

Since the electron-withdrawing force of the carbonyl oxygen causes the dipolar character of the pentadienone moiety[9] and its positive ends, which are linked to the annulated ring, induce the polar structure of the ring, the slightly positive-calculated net charges on the pentadienone moieties of **2** and **6** can be regarded as actually zero. This indicates that the polar structures of **2** and **6**, which have an annulated aromatic ring, are based on the local dipoles of penta-1,4-dien-3-one and the induced dipole of the annulated ring. Conversely, the negative net charges on the pentadienone moiety of the 8*H*-3-oxaheptalen-8-ones **3** and **5** reveal that their polarities are based not only on the local dipoles, but also on the partial intramolecular CT interaction from the olefinic oxepin ring to the pentadienone moiety.

This intramolecular CT interaction could be explained by the symmetry consideration as follows:

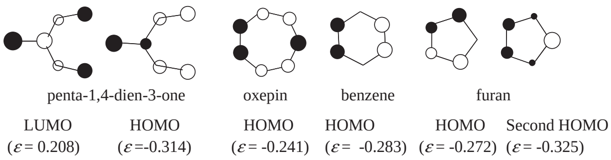


Fig. 3. Highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of penta-1,4-dien-3-one, oxepin, benzene, and furan, and their energy levels (au). HOMO and LUMO coefficients and their energy levels are calculated at the HF/STO-3G level.

1. As shown in Fig. 3, the LUMO of penta-1,4-dien-3-one interacts with the HOMO of oxepin and benzene, and also with the second HOMO, not the HOMO, of furan. The energy difference between LUMO and HOMO (or second HOMO of furan) is the smallest at the pair of oxepin and penta-1,4-dien-3-one, so the interaction between them may be the largest.

2. When comparing the net π-electron densities on the pentadienone moiety of **5**[10] with those of **2** and **6**, shown in Fig. 2, a marked increase of π-electron density due to intramolecular CT interaction of 8*H*-3-oxaheptalen-8-one is found on the carbonyl oxygen. This is attributed to the mixing of the HOMO of penta-1,4-dien-3-one with its LUMO through the HOMO of oxepin, i.e., the HOMO of 8*H*-3-oxaheptalen-8-one is represented approximately as follows:

$$\phi_{\text{HOMO}(8H\text{-3-oxaheptalen-8-one})} = \phi_{\text{HOMO(oxepin)}} - \phi_{\text{HOMO(penta-1,4-dien-3-one)}} + \phi_{\text{LUMO(penta-1,4-dien-3-one)}}. \quad (4)$$

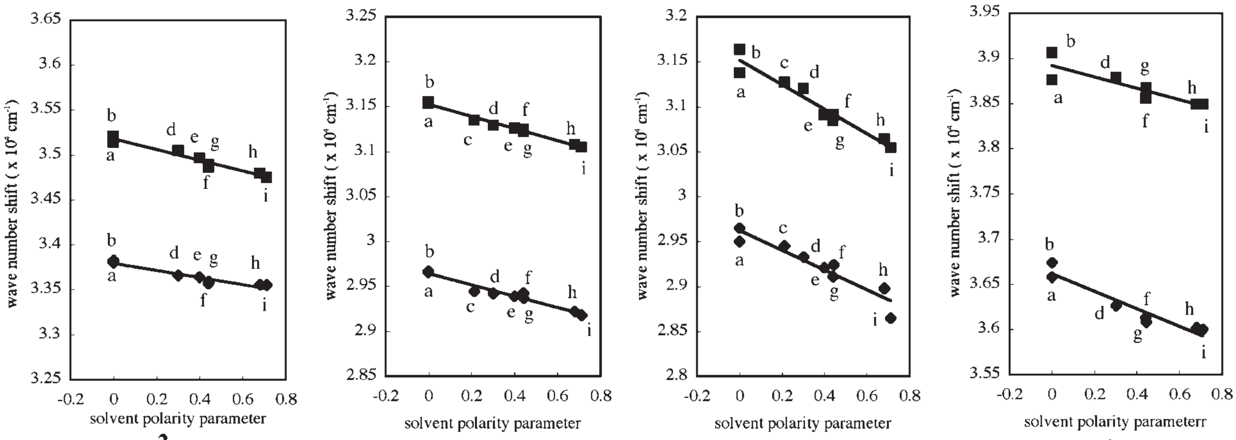
The Excited-State Dipole Moments of Furo[3,4-*d*]tropone (2), 8*H*-3-Oxaheptalen-8-one (3), Its 2,4-Dimethyl Derivative 5, and 4,5-Benzotropone (6). The dipole moments of the two lowest excited states of furo[3,4-*d*]tropone (**2**), 8*H*-3-oxaheptalen-8-one (**3**), its 2,4-dimethyl derivative **5** and 4,5-benzotropone (**6**) were determined using the McRae equation,[11] shown as follows.

$$\Delta\nu = (AL + B)\left[\frac{n^2 - 1}{2n^2 + 1}\right] + C\left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right] + F\left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right]^2. \quad (5)$$

$C = [2/hca^3](\mu_g - \mu_e)\mu_g$ a: effective cavity radius

μ_g, μ_e: dipole moment of the ground and the exited states

The equation describes the frequency shift ($\Delta\nu$) of a polar molecule in various solvents in terms of the solvent properties n (index of refraction) and D (dielectric constant). The study



2 **3** **5** **6**

Fig. 4. McRae plots for the annulated tropones **2**, **3**, **5**, and **6**; a: cyclohexane, b: hexane, c: dipropyl ether, d: diethyl ether, e: ethyl acetate, f: tetrahydrofuran, g: 1,2-dimethoxyethane, h: propiononitrile, i: acetonitrile.

Table 5. Effective Cavity Radii (Å) and Values, $[2/hca^3](\mu_g - \mu_e)\mu_g$ (cm^{-1}) and $(\mu_g - \mu_e)\mu_g$ (D^2), of Annulated Tropones **2**, **3**, **5**, and **6**

Compound	**2**	**3**	**5**	**6**
Cavity Radius/Å	4	5	5	4
First Excited				
$[2/hca^3](\mu_g - \mu_e)\mu_g/cm^{-1}$	-3.89×10^4	-6.33×10^4	-11.04×10^4	-9.57×10^4
$(\mu_g - \mu_e)\mu_g/D^2$	−2.48	−7.89	−13.75	−6.10
Second Excited				
$[2/hca^3](\mu_g - \mu_e)\mu_g/cm^{-1}$	-5.99×10^4	-6.68×10^4	-13.62×10^4	-6.21×10^4
$(\mu_g - \mu_e)\mu_g/D^2$	−3.82	−8.32	−16.97	−3.96

on the excited-state dipole moments of azulene[12] indicated reasonable assumptions for the equation; the constant F of the third term of the equation might be taken to be zero and the coefficient $(AL + B)$ of the first term could be considered to be constant in magnitude in polar and nonpolar solvents, suggesting that the first term of the equation should vary relatively slightly compared with the second term. Two absorption maxima in the longest wavelength band of the annulated tropones **2**, **3**, **5**, and **6** were measured in various solvents. The π–π^* transition energies (cm^{-1}) corresponding to two absorption maxima were plotted against the solvent polarity parameter of the second term of the equation $[(D - 1)/(D + 2)] - [(n^2 - 1)/(n^2 + 2)]$, as shown in Fig. 4, illustrating a good linear relationship between them.[13] The observed least-squares slopes of the lines in Fig. 4 correspond to the constant of the second term of the McRae equation, $C = [2/hca^3](\mu_g - \mu_e)\mu_g$. The effective cavity radius a, which is a measure of molecular size, is assumed to be 4 Å for **2** and **6**, and 5 Å for **3** and **5**, by reference to $a = 4$ Å for azulene having a similar framework to those of **2** and **6**.[12] From these values, the values, $[2/hca^3](\mu_g - \mu_e)\mu_g$ (cm^{-1}) and $(\mu_g - \mu_e)\mu_g$ (D^2) are obtained and are shown in Table 5. The observed and the calculated moments at the two lowest excited states are shown in Table 6. The calculation of the excited-state dipole moments were carried out by employing the CNDO/S CI method based on the geometry optimized with the PM3 method for **3** and those determined from the X-ray structures for **2**, **5**, and **6**.

Table 6. Observed and Calculated Dipole Moments (D) at Two Lowest Excited States of Annulated Tropones **2**, **3**, **5**, and **6**[a)]

Compound	**2**	**3**	**5**	**6**
First excited-state dipole moment/D				
Observed	4.48	6.47	8.20	5.98
Calculated	5.01	6.57	8.37	5.86
Second excited-state dipole moment/D				
Observed	4.83	6.56	8.75	5.52
Calculated	10.43	9.52	8.62	5.15

a) The excited-state dipole moments were calculated using the CNDO/S CI method, based on the geometry optimized with PM3 method for **3** and on the X-ray structures for **2**, **5**, and **6**.

The calculated dipole moments of the excited states are roughly in agreement with the observed data, except for the dipole moments of the second excited state of **2** and **3**. The moments of the ground and excited states are oriented in the same manner. The observed results, where the excited-state dipole moments are larger than those of the ground state, confirm the qualitative interpretation on the bathochromic shift of absorption spectra found in the solvent of increased polarity. As do other annulated tropones, naphtho[2,3-*d*]tropone and anthra[2,3-*d*]tropone also exhibit a similar bathochromic shift in the absorption spectra.[14] The larger dipole moments of the excited states might confer nonlinear optical properties on the annulated tropones.[15]

Table 7. Two Absorption Maxima (nm) at the Longest Wavelengths of Annulated Tropones **2**, **3**, **5**, and **6**

Solvent	Compound			
	2	**3**	**5**	**6**
Acetonitrile	298.1, 287.8	342.7, 322.1	349.1, 327.4	277.8, 259.8
Propiononitrile	298.0, 287.4	342.2, 321.7	345.1, 326.4	277.6, 259.8
1,2-Dimethoxyethane	297.7, 286.6	339.8, 320.3	342.0, 323.5	277.2, 258.6
Tetrahydrofuran	297.9, 286.9	340.5, 320.0	343.5, 324.3	276.8, 259.4
Ethyl acetate	297.3, 286.0	340.3, 319.9	342.3, 323.5	
Diethyl ether	297.1, 285.3	339.9, 319.6	341.0, 320.5	275.8, 257.8
Dipropyl ether		339.6, 319.0	339.6, 319.8	
Hexane	295.6, 284.0	337.0, 317.0	337.3, 316.1	272.2, 256.0
Cyclohexane	295.9, 284.6	337.2, 317.1	339.0, 318.7	273.4, 258.0

Conclusion

The tropone rings of furo[3,4-*d*]tropone (**2**), 2,4-dimethyl-8*H*-3-oxaheptalen-8-one (**5**), and 4,5-benzotropone (**6**) have a somewhat shallow boat form with clear bond alternation. The polar structures of **2** and **6**, which have an aromatic annulated ring, are based on the local dipole of the pentadienone moiety and the induced dipole of the annulated ring, while those of 8*H*-3-oxaheptalen-8-one (**3**) and its 2,4-dimethyl derivative **5** are based not only on the local dipoles, but also on the partial intramolecular CT interaction from the olefinic oxepin ring to the pentadienone moiety. The dipole moments of the two lowest excited states of the annulated tropones **2**, **3**, **5**, and **6** are all oriented in the same direction as that of the ground state, but have greater magnitudes.

Experimental

Materials. Analytically pure samples of furo[3,4-*d*]tropone (**2**), 8*H*-3-oxaheptalen-8-one (**3**), and 2-methyl- and 2,4-dimethyl-8*H*-3-oxaheptalen-8-ones (**4**) and (**5**) were prepared according to the synthetic methods reported by us.[2,3] 4,5-Benzotropone (**6**) and 2,7-dimethyloxepin were prepared according to the literatures.[16,17]

Measurement of the Ground-State Dipole Moments. The dipole moments were determined by measuring the dielectric constant and the density of several dilute solutions of the sample. The dielectric constants of the dilute solutions were measured at 25 ± 0.1 °C on a home-made apparatus (high-frequency bridge method). The densities of the dilute solutions were also measured at 25 ± 0.1 °C using an Ostwald-type pycnometer. Benzene, which was carefully purified, was used as a solvent, and samples synthesized were purified by recrystallization from suitable solvents before measurements. The range of concentrations of the solutes was from about 0.4×10^{-4} to 2.5×10^{-3} weight fraction.

Calculation of the Ground-State Dipole Moments. The dipole moments of the ground states were calculated by using the program package Gaussian 98.[18] For the calculations, three types of methods, i.e., HF, MP2, and B3LYP methods, were used. For all calculations, the basis set 6-311G** was employed and the molecular structures, except for 8*H*-3-oxaheptalen-8-one (**3**), were used which were obtained experimentally from the X-ray analysis. In the case of 8*H*-3-oxaheptalen-8-one (**3**), the molecular structure was optimized by the B3LYP and HF methods.

Measurement of Two Absorption Maxima at the Longest Wavelength of the Annulated Tropones 2, 3, 5, and 6. The absorption spectra of the annulated tropones **2**, **3**, **5**, and **6** were measured in spectral-grade solvents on a Beckman DU 600 spectrometer. There are two π–π^* transitions in the longest wavelength band of **2**, **3**, **5**, and **6**. The absorption bands of **3** and **5** at the longest wavelength were resolved by a curve-fitting procedure using the Gaussian function. 4,5-Benzotropone (**6**) exhibits one absorption band of longer wavelength, which was divided into a positive and a negative band in the magnetic circular dichroism (MCD) spectra. The MCD spectra were recorded on a Jasco J-600C spectropolarimeter with a 1.32-T electromagnet. Two absorption maxima observed from the spectra in a number of polar and nonpolar solvents are shown in Table 7.

Calculation of the Excited-State Dipole Moments. The excited-state dipole moments were calculated according to references on the CNDO/S method[19] and PM3 method.[20]

X-ray Crystallographic Study. Crystal data: for compound **2**, $C_9H_6O_2$, monoclinic, $a = 3.839(4)$, $b = 7.451(9)$, $c = 12.037(7)$ Å, $\beta = 100.30(4)^\circ$, $V = 338.7(6)$ Å^3, $T = 150$ K, space group Pn (No. 7), $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.102\,\text{cm}^{-1}$, 3052 reflections measured, 753 unique ($R_{\text{int}} = 0.036$) used in all calculations, final $R1 = 0.034(2\sigma > F^2)$ and $Rw(F^2) = 0.078$ (all data), GOF = 1.014; for compound **5**, $C_{13}H_{12}O_2$, orthorhombic, $a = 7.456(2)$, $b = 21.365(5)$, $c = 12.813(3)$ Å, $V = 2041.1(8)$ Å^3, $T = 150$ K, space group $Pbca$ (No. 61), $Z = 8$, $\mu(\text{Mo K}\alpha) = 0.087\,\text{cm}^{-1}$, 19324 reflections measured, 2207 unique ($R_{\text{int}} = 0.023$) used in all calculations, final $R1 = 0.039(2\sigma > F^2)$ and $Rw(F^2) = 0.095$ (all data), GOF = 1.088; for compound **6**, $C_{11}H_8O$, monoclinic, $a = 6.226(2)$, $b = 7.633(2)$, $c = 17.080(5)$ Å, $\beta = 100.847(5)^\circ$, $V = 797.2(4)$ Å^3, $T = 150$ K, space group $P2_1/n$ (No. 14), $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.082\,\text{cm}^{-1}$, 6735 reflections measured, 1520 unique ($R_{\text{int}} = 0.022$) used in all calculations, final $R1 = 0.0410(2\sigma > F^2)$ and $Rw(F^2) = 0.0998$ (all data), GOF = 1.059. Reflection data for three compounds were collected on a Rigaku CCD diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å) and refined by full-matrix least-squares on F^2 using SHELXL 97.[21] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-290950, -290951, and -290952 for compounds **2**, **5**, and **6**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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