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Experimental and Computational Studies on the Dipole Moments of Annulated-Tropones and 1,4-Polyacenequinones

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From both the experimental and computational perspectives, we examined the annulation effects of benzene rings on the ground-state dipole moment for two series of conjugated ketones. The first is a series of tropones (**1**), 4,5-benzotropone (**2**), 4,5-naphthotropone (**3**), 4,5-anthratropone (**4**), 4,5-tetracenotropone (**5**), and 4,5-pentacenotropone (**6**). The second is a series of 1,4-benzoquinones (**7**), 1,4-naphthoquinone (**8**), 1,4-anthraquinone (**9**), 1,4-tetracenequinone (**10**), 1,4-pentacenequinone (**11**), 1,4-hexacenequinone (**12**), and 5,12-tetracenequinone (**13**). Among these compounds, we determined the ground-state dipole moments of compounds **3**, **9**, **10**, and **13** experimentally as 5.19, 2.07, 2.95, and 1.33 D, respectively. The ground-state dipole moments of the above two series were calculated by Hartree–Fock (HF), density functional theory (DFT), and Møller–Plesset second-order perturbation (MP2) methods. We examined the ground-state dipole moments of the two series to determine whether they converge to a limit. From the MP2 calculations, we estimated the converged dipole moments of annulated-tropones and 1,4-polyacenequinone, as 7.58 and 6.17 D, respectively.

The electric dipole moment of a molecule is very important for studying molecular electronic structures and properties of both ground- and excited-states. Especially, it is invaluable to know the ground-state dipole moment in order to determine the excited-state dipole moment of a molecule by spectroscopic methods. Moreover, knowing both the ground- and excited-state dipole moments, is useful for estimating nonlinear optical constants, since the change of the dipole moment between the ground and excited states is involved in the third-order nonlinear optical constant. In this work, we studied the ground-state dipole moments of conjugated ketones i.e., tropone (**1**), 1,4-naphthoquinone (**8**), and their benzene-annulated compounds. The ground-state dipole moments of many carbonyl compounds are about 2.5 D which is approximately equal to that of **14**. Cyclopropenone (**15**), however, has a large dipole moment of 4.39 D.[1] This value is unsurprisingly far larger than the ground-state dipole moment, 1.9 D, of methylenecyclopropene (**16**).[2] In compound **15**, the π-electron system forms T-type conjugation and this compound is the simplest cyclic ketone (Scheme 1). Many chemist have studied this simple cyclic system from both experimental and theoretical points of view.[3,4] Najafian et al. also studied some ketocyclopolyenes with respect to aromatic properties by theoretical methods.[5] Interestingly, Hollis et al. reported that compound **15** was found as the first cyclic molecule among interstellar compounds recently.[6] Aldehyde compounds have been also known as metabolic intermediates.

Recently, we have studied the molecular structures and dipole moments of tropones annulated with furan, benzene, and oxepin from both experimental by X-ray analysis and theoretical perspectives.[7] In these studies we have determined the dipole moments of both the ground- and excited-states of 4,5-benzotropone (**2**) experimentally, and confirmed the values from molecular orbital calculations by using MP2 and CNDO/S CI methods for ground- and excited-states, respectively. In this work, in order to examine the annulation effects of benzene rings on the ground-state dipole moment of tropone, we synthesized a series of tropones annulated with benzene, i.e., 4,5-benzotropone (**2**), 4,5-naphthotropone (**3**), and 4,5-anthratropone (**4**). In addition we determined the dipole moment of **3** experimentally. The dipole moment of compound **3** is reported for the first time in this work. However, unfortunately we could not determine the dipole moment of **4** due to insolubility in benzene.[8] In order to confirm the dipole moments determined experimentally and to examine the annulation effect of the benzene ring on compound **1**, we performed HF, DFT, and MP2 calculations for **1** to **4**, and 4,5-tetracenotropone (**5**) and 4,5-pentacenotropone (**6**) which were annulated successively to compound **4** with one or two benzene rings, respectively (we abbreviate these compounds hereafter as tropone-series).

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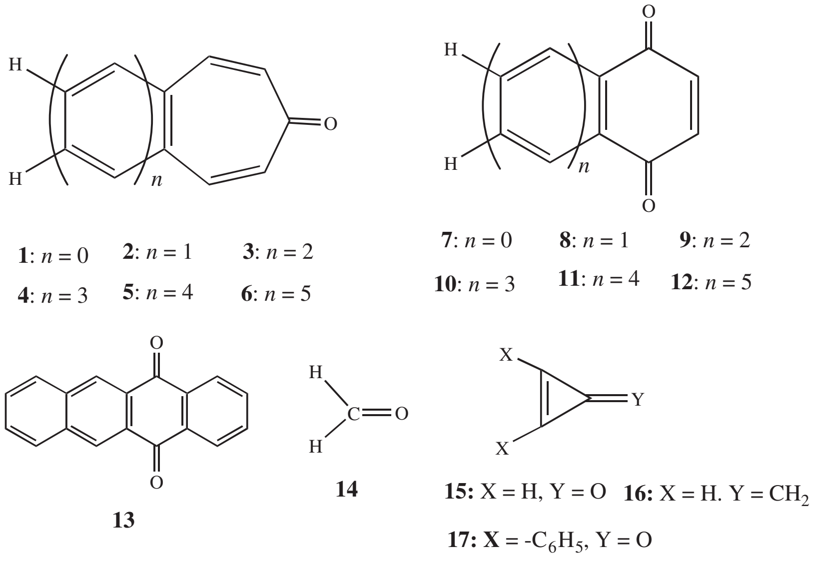


Scheme 1.

Furthermore, we examined the properties of another type of π-electron system for the comparison with the above-mentioned compounds (tropone-series) 1,4-polyacenequinone series in which two carbonyl groups conjugate with polyacene, i.e., 1,4-naphthoquinone (**8**), 1,4-anthraquinone (**9**), 1,4-tetracenequinone (**10**), 1,4-pentacenequinone (**11**), 1,4-hexacenequinone (**12**), and 5,12-tetracenequinone (**13**) (we abbreviate these compounds as 1,4-quinone-series). The *para*-quinone is known as an aromatic compound in natural products. The photochemical properties of quinones have been studied also since these compounds are good natural dyes. We studied the electronic properties and the IR spectra of **8** and its hydroxy-derivatives.[9] We also determined the dipole moments of both ground- and some lower excited-states of compound **8** and its derivatives by spectroscopic and theoretical methods. Furthermore we discuss the correlation between the substituent and the dipole moments of **8** and its derivative substitutions.[10] It is interesting to study the behavior of the ground-state dipole moments of 1,4-polyacenequinones with no substituent, since the ground-state dipole moment will be affected only by the annulation of the benzene ring. For polyacenequinone, Yamaji et al. reported photochemical properties of **10** (1,4-tetracenequinone) recently.[11] They estimated the excited-state dipole moment of **10** to be 13.0 D, and concluded that this large value originated from the aromatic subsystem. In order to estimate the excited-state dipole moment however, it was necessary to know the ground-state dipole moment. They used 2.5 D as the ground-state dipole moment of **10** which was obtained from semi-empirical MO calculations. To obtain reliable excited-state dipole moments we need to provide more precise ground-state dipole moments. We determined the ground-state dipole moments of **9**, **10**, and **13** for the first time in this work as well as **3**, experimentally. The effect of benzene ring annulation of compound **8** was also examined by theoretical calculations as was the case with the tropone-series.

Here, we determined the ground-state dipole moments of **3**, **9**, **10**, and **13** experimentally. We furthermore calculated the ground-state dipole moments of two series (**1**–**6** and **8**–**13**) by sophisticated methods such as HF, DFT, and MP2 methods. We examined the ground-state dipole moments of the two series to determine whether they converge to a limit, and estimated the limit dipole moments of the systems, i.e., benzene-annulated tropones **2**–**6** and 1,4-polyacenequinones **8**–**13**, as 7.58 and 6.17 D by MP2 calculations, respectively.

Experimental and Calculations

Materials. Analytically pure samples of naphthotropone (**3**), and 1,4-anthraquinone (**9**), 1,4-tetracenequinone (**10**), and 5,12-tetracenequinone (**13**) were prepared according to the literature.[12,13]

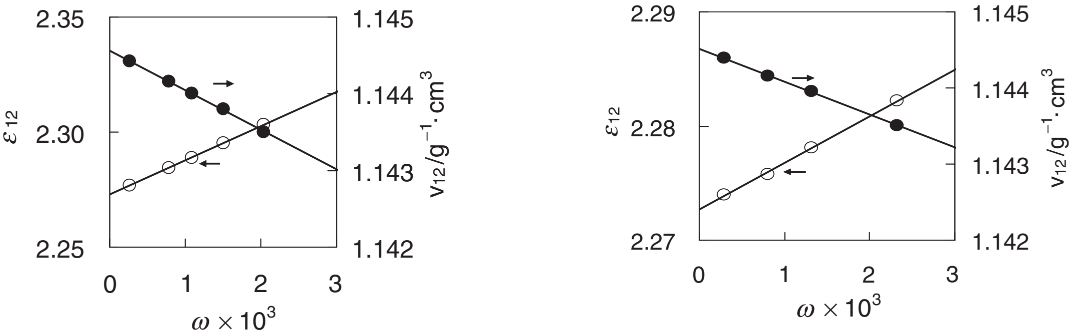
Measurement of the Ground-State Dipole Moments. The ground-state dipole moments of the compounds were determined by measuring the dielectric constant and density of several dilute solutions of the sample. The dielectric constant of the dilute solutions was measured at 25 ± 0.1 °C on a home-made apparatus (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.

The dipole moments of the molecules were determined from the following equation at temperature T in Debye units:[14]

$$\boldsymbol{\mu} = 0.01281[(P_{2\infty} - R_{\mathrm{MD}})T]^{1/2} \tag{1}$$

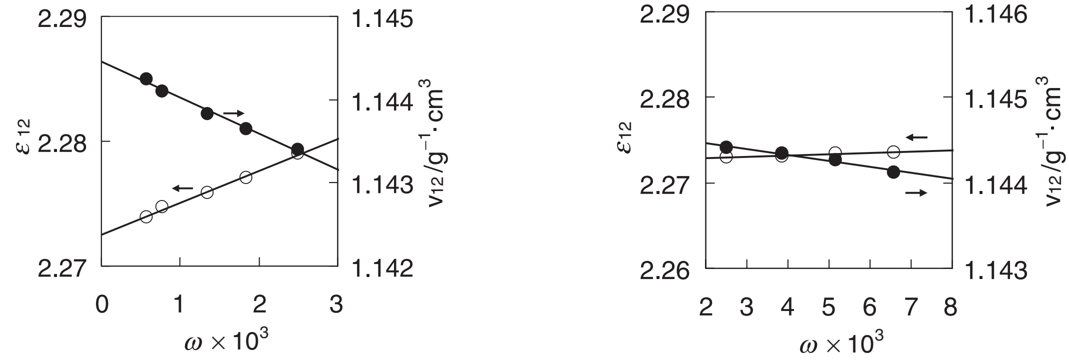
in which $P_{2\infty}$ and R_{MD} mean the total polarization of the solute at infinite dilution and the molecular refraction, respectively. The molecular refraction R_{MD} suffers from the contribution of bond refraction and atomic polarization, although that of atomic polarization is relatively small and its precise estimation is difficult.[15] In this work, the R_{MD} are evaluated from the sum of the bond refractions, i.e., 1.676, 1.296, 4.17, and 3.32 cm^3 for C–H, C–C, C=C, and C=O bonds, respectively.[16] The total polarization of the solute at infinite dilution was determined by using the method of Halverstadt and Kumler based on the following equation:[17]

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



(a): Compound **3**

(c): Compound **10**



(b): Compound **9**

(d): Compound **13**

Figure 1. The relationship of dielectric constants ε_{12} and specific volumes v_{12} vs. weight fractions ω_{12} for compounds **3**, **9**, **10**, and **13**.

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:

$$\varepsilon_{12} = \varepsilon_1 + \alpha\omega_2 \tag{3}$$

$$v_{12} = v_1 + \beta\omega_2 \tag{4}$$

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 eq 2 using the experimental data described above.

Calculations of the Ground-State Dipole Moments. The ground-states dipole moments of the compounds studied here were calculated by using the program package Gaussian 98.[18] For the calculations, three methods, HF, DFT(B3LYP), and MP2 were used, and the basis set 6-311G** was employed for all calculations. The calculations were performed at the Information Center of Hirosaki University, the Research Center for Computational Science (Okazaki, Japan) and Synergy Center of Tohoku University.

Results and Discussion

Experimental Results. Figures 1a–1d show the dielectric constants, ε_{12}, and specific volumes, v_{12}, of compounds **3**, **9**, **10**, and **13** for various weight fractions, ω_2, respectively. The parameters α, β, ε_1, and v_1 in eqs 3 and 4 were obtained by the least-squares fitting of the relationships eqs 3 and 4 as shown in Figures 1a to 1d. The total polarizations, $P_{2\infty}$, calculated from eq 2 and molar refractions, R_{MD}, obtained by using the above-mentioned bond-refractions for the sodium D line, of the solutes are shown in Table 1 along with the values, α, β, ε_1, and v_1. The ground-state dipole moments of **3**, **9**, **10**, and **13**, were obtained from eq 1 using $P_{2\infty}$ and R_{MD} which are given in Table 1, and are also shown in Table 1. Unfortunately we could not obtain the experimental dipole moments for compounds **4**, **5**, and **6** (**5** and **6** have not yet been synthesized.). Since the solubility of **4** in benzene was too low to measure the dielectric constants, we could not determine the ground-state dipole moment of this compound. The dipole moments of organic compounds which are expressed as the molecular formula C_nH_mO, i.e., having only one functional group as the carbonyl and excluding other functional groups such as hydroxy and ether, are given for about one hundred compounds in McClellan's Table.[19] The dipole moments of these carbonyl compounds ranged from 2.3 to 4.5 D, but one exception was found to be 5.08 D which was the largest in the above-mentioned group. This molecule is 2,3-diphenylcyclopropenone (**17**) (In McClellan's Table, 2,3-diphenylcyclopropanone also showed 5.08 D, but this was a misprint perhaps.). The dipole moments of unsaturated-cycloketones are typically larger than those of corresponding saturated-cycloketones or aldehydes. It may be considered that the π-electron system plays an important role in these compounds. Our experimental results for **2** and **3** fell out of the above range. The ground-state dipole moment of compound **3** is 5.19 D and is larger than that of **17** and also **2**. The ground-state

Table 1. Parameters (α, β), Dielectric Constant (ε_1), Specific Volume (v_1), Molar Refraction (R_{MD}), Polarization ($P_{2\infty}$), and Dipole Moments of Compounds **3**, **9**, **10**, and **13**

Compound	α	$\beta/\mathrm{cm^3\,g^{-1}}$	ε_1	$v_1/\mathrm{cm^3\,g^{-1}}$	$R_{\mathrm{MD}}/\mathrm{cm^3}$	$P_{2\infty}/\mathrm{cm^3}$	$\boldsymbol{\mu}/\mathrm{D}$
3	14.812	−0.516	2.2729	1.14456	62.21	613.14	5.19
9	2.624	−0.442	2.2724	1.14448	58.028	146.3305	2.07
10	4.065	−0.43	2.2727	1.14451	73.608	252.429	2.95
13	1.547	−0.695	2.2726	1.1446	73.608	109.745	1.33

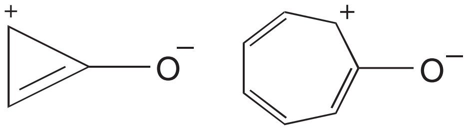
Table 2. Ground-State Dipole Moments of Compounds **1**–**6** and **8**–**13** (/D)

Compounds	HF /6-311G**	B3LYP /6-311G**	MP2 /6-311G**	Explt.
1	4.49	4.42	4.12	4.25[a)]
2	5.2	5.16	4.65	4.67[b)]
3	5.73	5.76	5.1	5.19
4	6.13	6.25	5.49	—
5	6.45	6.67	5.81	—
6	6.69	7.03	6.07	—
8	1.08	1.14	1.20	1.21[c)], 1.33[d)]
9	1.95	2.2	2.21	2.07
10	2.61	3.11	3.00	2.95
11	3.1	3.89	3.63	—
12	3.48	4.56	4.13	—
13	0.86	1.02	1.00	1.33

a) Ref. 20. b) Ref. 5. c) Ref. 21. d) Ref. 9b.

dipole moment of compound **13** can be explained qualitatively as a vector sum of that of compounds **8** and **9**, i.e., $\boldsymbol{\mu}(\mathbf{13}) \approx 2.07\,\mathrm{D}$ ($\boldsymbol{\mu}(\mathbf{9})$)–1.21 D ($\boldsymbol{\mu}(\mathbf{8})$). The results were compared with the calculated values and are discussed along with the other compounds shown below.

The Results of Calculations. Tropone-Series: The calculated ground-state dipole moments of **1** to **6** are given in Table 2 along with the experimental ground-state dipole moments. Unfortunately, we could not obtain the experimental dipole moments for compounds **4**, **5**, and **6** (**5** and **6** have not yet been synthesized.), since the solubility of compound **4** in benzene is too low to measure the dielectric constants. In all calculations we assumed that the compounds are planar. The molecular geometrical parameters were all optimized in each calculation. The ground-state dipole moments calculated by MP2 gave the best correspondence to the experimental dipole moments for compounds **1, 2**, and **3** among three methods. The ground-state dipole moment of compound **1** has been reported by many authors as 4.30,[22] 4.17,[23] and 3.71 D.[24] We obtained the ground-state dipole moment of **1** as 4.20 D in benzene solution experimentally and it was similar to that of **15**.[25] Bertelli and Andrews[26] analyzed the ground-state dipole moment of **1**, comparing it with those of 4,4-dimethylcyclohexa-2,5-dienone ($\boldsymbol{\mu} = 3.66\,\mathrm{D}$), cyclohepta-2,6-dienone ($\boldsymbol{\mu} = 4.04\,\mathrm{D}$), and several related compounds, in conjunction with the molecular orbital (MO) calculations, and indicated that the ground state of **1** was adequately described as polyenone. This result derived from the analysis of the ground-state dipole moment, agrees with X-ray structural analysis[20] and our calculated result. A cata-condensation of a benzene ring to polar tropone (**1**) or annulated tropones produces a large conjugated system, which exhibits larger dipole moment.



Scheme 2.

Bachrach and Liu discussed **15** on the basis of the resonance structure or π-electron delocalization.[4] The dipole moment of **1** is slightly smaller than that of **15** in spite of having a large conjugate system. This fact was explained by using the limiting valence ionic-structures (Scheme 2). That is, the possible numbers of ionic structures of **1** are much more than those of **15**, nevertheless the ground-state dipole moments of these compounds do not differ greatly. This suggests that the contribution of the ionic structure of compound **1** is less than that of **15** and the molecular structure of **1** is described as polyenone mentioned above.

Carbonyl dipole moment was assumed to be about 2.5 D, as has often been discussed.[27] This value, however, is too small and not adequate for cyclic-conjugated systems with a C=O group. Shimozawa et al. assumed the moment of C=O in tropone (**1**) to be 4.0 D, and applied this value to the determination of the position of halogeno-substitution from the dipole moments of some halogeno-2,3-benzotropones, and were able to illustrate a good relationship between the experimental and calculated dipole moments.[28] For 4,5-benzotropone they estimated the contribution of the benzene ring to be 0.8 D which was somewhat large for explaining the present work. If we apply these values to the present compounds, our experimental value, 4.67 D, of 4,5-benzotropone is well explained. In this work we will not discuss the carbonyl group moment in detail. Instead of the carbonyl group moment we aim toward the annulation effect of benzene rings.

The calculated ground-state dipole moments of the annulated tropone, $\boldsymbol{\mu}$, may be expressed as eq 5

$$\boldsymbol{\mu}_n = \boldsymbol{\mu}_i + \sum_i^n \Delta\boldsymbol{\mu}_i \tag{5}$$

where n is the number of benzene rings and $\Delta\boldsymbol{\mu}_i$ is the increment of the dipole moment due to the annulation of a benzene ring, i.e., $\Delta\boldsymbol{\mu}_i = \boldsymbol{\mu}_{i+1} - \boldsymbol{\mu}_i$. If the variable n is assumed to be continuous, the dipole moment will be given as the following equation.

$$\boldsymbol{\mu}_n = \boldsymbol{\mu}_i + \int_i^n \Delta\boldsymbol{\mu}\mathrm{d}n \tag{6}$$

Figure 2a shows the behavior of $\Delta\boldsymbol{\mu}$ with respect to n for the MP2 calculations. From the curve fitting, we get the relation-

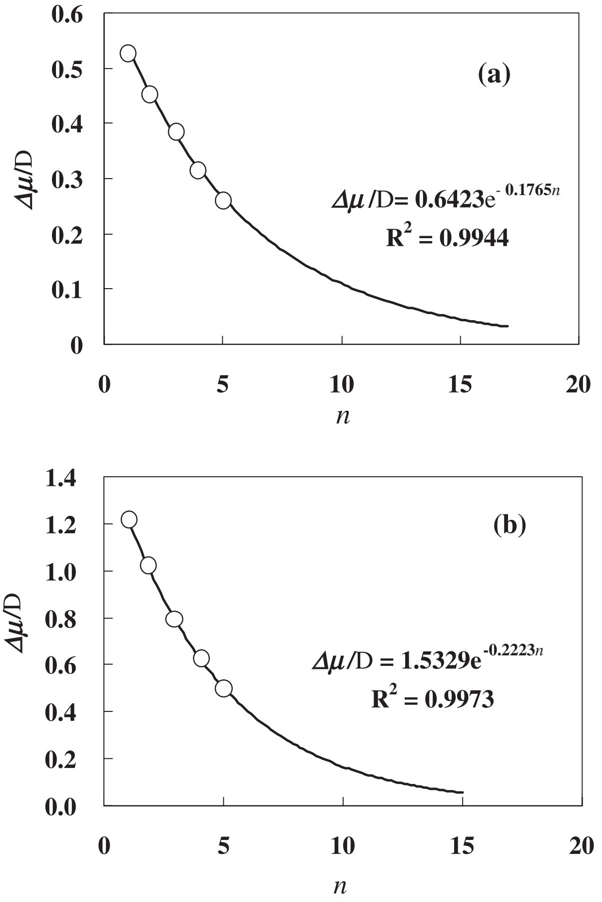


Figure 2. The relationship between the increment of dipole moment $\Delta\boldsymbol{\mu}$ and the number of benzene rings n. (**a**): Tropone-series, (**b**): 1,4-Quinone-series.

ship between $\Delta\boldsymbol{\mu}$ and n as follows;

$$\Delta\boldsymbol{\mu} = 0.6423\mathrm{e}^{-0.1765n} \tag{7}$$

for the tropone-series. Using the above equations we obtained the relationship between $\boldsymbol{\mu}_n$ and n from the postulate of eq 6 as given below,

$$\boldsymbol{\mu}_n = \boldsymbol{\mu}_i + 3.6391\mathrm{e}^{-0.1765i} - 3.6391\mathrm{e}^{-0.1765n} \tag{8}$$

Equation 8 suggests that the ground-state dipole moment of the tropone-series converges to a limit, since the third term of eq 8 approaches zero as n approaches infinity. From eq 8 we obtained the estimated limit value of the dipole moment as 7.58 D by the MP2 method, by using the values $\boldsymbol{\mu}_5 = 6.07$ D and $i = 5$. We also obtained the limit dipole moments of this series as 7.59 and 8.99 D by the HF and B3LYP calculations, respectively.[29] These are very large values, and large polarization is expected in the electronic ground-state of these molecules. For molecular design, these results present a fascinating target in that these compounds may be possibly used as nonlinear optical materials.[30]

1,4-Quinone-Series: The calculated ground-state dipole moments are given in Table 2 along with the experimental dipole moments. In our calculations, as was the case with the tropone-series, the MP2 level calculations gave the best correspondence to the experimental dipole moments for **8, 9,** and **10**. The difference between the dipole moments calculated by B3LYP and by MP2 methods became larger and larger with increasing number of benzene rings. For the tropone-series, the B3LYP calculations gave somewhat exaggerated dipole moments here for large systems such as compounds **8** and **9**.

We estimated the converged dipole moment of this series, in a similar manner to the tropone-series. The increment of the dipole moment, $\Delta\boldsymbol{\mu}$, is expressed by the following eq 9 from the curve fitting as given in Figure 2b for the MP2 calculations,

$$\Delta\boldsymbol{\mu} = 1.5329\mathrm{e}^{-0.2223n} \tag{9}$$

The dipole moment $\boldsymbol{\mu}_n$ is expressed for 1,4-quinone-series as follows;

$$\boldsymbol{\mu}_n = \boldsymbol{\mu}_i + 6.8956\mathrm{e}^{-0.2223i} - 6.8956\mathrm{e}^{-0.2223n} \tag{10}$$

By using the values $\boldsymbol{\mu}_5 = 4.13$ D and $i = 5$, we obtained the converged dipole moment of this series as 6.17 D which was appreciably large and near that of the tropone-series. We also obtained the converged dipole moments of this series as 4.91 and 9.53 D for the HF and B3LYP methods, respectively.[31] It may be fortuitous that the limit dipole moments of the B3LYP calculations are similar for the two series as compared with the other two calculations.

Conclusion

The ground-state dipole moments of carbonyl compounds naphthotropone (**3**), 1,4-anthraquinone (**9**), 1,4-tetracenequinone (**10**), and 5,12-tetracenequinone (**13**) were determined experimentally for the first time, and will be useful for the study of molecular interactions in solution and excited-states. The effect of benzene ring annuluation to tropone and 1,4-benzoquinone on the ground-state dipole moments were examined from the HF, DFT, and MP2 calculations. The ground-state dipole moments for the two series were expected to converge to a limit as deduced from the incremental behavior of the dipole moment resulting from annulation with benzene rings. We estimated limit values to be about 7.58 and 6.17 D for the tropone- and 1,4-benzoquinone-series from the MP2 calculations, respectively. These values are large and are expected to be useful for designing nonlinear optical materials.

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8 The detail of the synthesis and spectroscopic properties of compounds **3** and **4** will appear elsewhere.

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