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Tropothione *versus* Tropone: A Comparison of the Charge Separation in the Ground State

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Abstract: The electric dipole moment of tropothione (**1**), a thiocarbonyl compound, and tropone (**2**), a carbonyl one, has been compared. The charge separation of **1** and **2** is evaluated on the basis of the dipole moment and ab initio calculations. The dipole moment (μ) of **1** is measured to be 4.42 D in carbon tetrachloride at −15 °C and is larger than that (μ = 3.71 D) of **2**. Ab initio molecular orbital calculations have reproduced these values well and have revealed the origin of this difference.

The experimentally determined electric dipole moment is one of the most direct quantitative measures of charge separation in the ground state of a molecule.[1] Correlations of the dipole moment and the theoretically calculated electron distributions provide a means of assessing π-electron delocalization, which is predicted to be dependent on charge separation for nonbenzenoid aromatic tropone.

Tropone (**2**) has received great attention because of the potential aromaticity due to Hückel $(4n + 2)\pi$ rule.[2] The resonance stability of tropone has been ascribed to the relative importance of the polar structure of **2b**.[3] In accordance with the reason, tropone has been recognized to have a large value of the dipole moment over the four decades. But, such the large aromaticity received a question on the basis of ^{1}H NMR vicinal coupling constants through a simulation analysis.[4] Giacomo and Smyth reported the first dipole-moment observation for tropone, 4.30 D.[5] In a later year, Kurita et al. reported a revised value, 4.17 D.[6]

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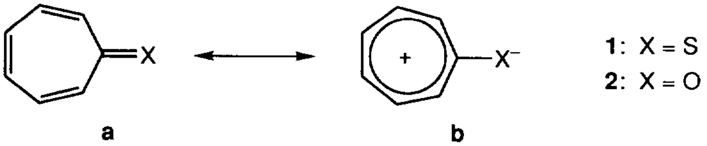
The latter value has been the standard for nonbenzenoid aromatic compounds and has been cited extensively in the literatures.



Thioketones are unstable compounds unless they are stabilized thermodynamically with heteroatoms or kinetically with bulky groups.[7] Especially, unsaturated thioketones are known to be more unstable. Our synthesis and isolation of tropothione (**1**),[8] the sulfur analogue of tropone (**2**), prompted us to determine the exact value of the ground-state electric dipole moment. Tropothione has been crystallized as a labile and deep red compound different from tropone. The potential instability of tropothione has prohibited observation of its substantial properties.

Replacement of the exocyclic oxygen in tropones to the sulfur atom forms a new family of tropothione (cycloheptatrienethione) derivatives.[9] Both **1** and **2** have the same ring skeleton and number of π-electrons but differ in the bond length of the exocyclic linkage, polarity and aromaticity. The effect of this atomic mutation has been subject to theoretical and experimental interest.[10] Since tropothione (**1**) is a novel (nonbenzenoid) aromatic compounds,[3] it is important to obtain the accurate value of the electric dipole moment against the thermal instability.[11] The electronegativity of the sulfur atom (2.5) is smaller than that of the oxygen one (3.5).[12] Consequently, contribution of dipolar resonance structure **1b** is expected to be not so large as that of **2b**. In this respect, the dipole moment of **2** appears to be larger than that of **1**. This paper describes evaluation of charge separations for tropothione and tropone on the basis of the dipole moment and high-level ab initio calculations.

RESULTS AND DISCUSSION

Dipole Moment of Tropothione (1) and Tropone (2).

Crystals of tropothione (**1**) are converted rapidly even at 0 °C (below the melting temperature of 20 °C) to a dimeric substance,[11] and concentrated solutions [$t_{1/2}$ (25 °C, 1.00 mol/L) 9.1 h] deteriorate within several hours at room temperature. However, a dilute solution of tropothione has a relatively long half-life time [$t_{1/2}$ (25 °C, 0.010 mol/L) 10.4 days; $t_{1/2}$ (25 °C, 0.001 mol/L) 38.0 days].[8] To prevent such a spontaneous decomposition of the material at 0 °C, we have performed the measurement in dilute solutions at the low temperature of −15 °C. Dilute solutions of **1** used in this report were sufficiently stable enough for the measurement at the low temperatures. It was confirmed that no decomposition of **1** was observed at the temperature by the Fourier-transform ^{1}H NMR spectroscopic monitoring and UV–visible detection before and after the measurements; the solutions used did not deteriorate during the experiments.

Under such careful conditions, we observed the dielectric constants (ε) of the dilute solutions of tropothione (**1**) as well as those of tropone (**2**) with six different mole fractions with a heterodyne beat apparatus. Table 1 summarizes the results observed for both tropothione and tropone. We obtained the molecular polarization of the solute from the experimental data by the method of Halverstadt and Kumler.[13] The measured values of the dielectric constants (ε_{12}), and densities (d_{12}) of the solutions were found to be linear functions of the weight fractions (w_2) of the solutes according to the equations, $\varepsilon_{12} = \varepsilon_1 + \alpha w_2$ and $d_{12} = d_1 + \beta w_2$. Table 2 lists the calculated results for both the compounds. The dipole moments were then obtained as follows. The total polarization ($P_{2\infty}$) is calculated for an extrapolation to an infinite dilution of **1** in carbon tetrachloride at −15.0 ± 0.05 °C based on the following equation:

$$P_{2\infty} = M_2 \left[\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \cdot \frac{1}{\alpha_1} \left\{ 1 + \frac{3\alpha}{(\varepsilon_1 - 1)(\varepsilon_1 + 2)} - \frac{\beta}{d_1} \right\} \right]$$

in which ε_1 is the dielectric constant, d_1 is the density of the solution, and M_2 is the molar mass. We obtained the P_∞ for tropothione and determined the dipole moment value by the Debye equation in Debye unit from the equation, $\mu = 0.01281[(P_{2\infty} - 1.05R_{MD})T]^{1/2}$. The total polarizations were observed to be 502.60 and 314.02 cm^3 for tropothione (**1**) and tropone (**2**), respectively, while the summations of the electronic and atomic polarizations were calculated to be 41.64 and 32.62 cm^3 for **1** and **2**, respectively.

Table 1. Weight Fractions (w_2) of the Solutes (**1**) vs. Dielectric Constant (ε_{12}) and Density (d_{12}).

Tropothione (**1**) [a]			Tropone (**2**) [b]		
$w_2 \times 10^5$	ε_{12}	d_{12} / (g cm^{-3})	$w_2 \times 10^5$	ε_{12}	d_{12} / (g cm^{-3})
0	2.2798	1.61034	0	2.2284	1.58553
168	2.3454	1.61082	618	2.3923	1.58681
302	2.3975	1.61127	1201	2.5464	1.58834
455	2.4573	1.61178	1554	2.6399	1.58901
609	2.5171	1.61229	2003	2.7588	1.59019
751	2.5727	1.61277	2498	2.8902	1.59133

[a] Measured at −15 °C. [b] Measured at 25 °C.

Table 2. Empirical Constants (ε_1, d_1, α, and β), Total Polarization ($P_{2\infty}$) of the Solutes, Molar Refractions (R_{MD}) for the D Sodium Line, and Dipole Moments (μ).

		ε_1	d_1 / g cm^{-3}	α	β / g cm^{-3}	$P_{2\infty}$ / cm^3	R_{MD} / cm^3	μ / D[a]
1	Tropothione [b]	2.2798	1.6103	38.987	0.3262	502.60	39.66	4.42 ± 0.01
2	Tropone [c]	2.2284	1.5855	26.485	0.2341	314.02	31.07	3.71 ± 0.01

[a] 1 D = 3.3356 × 10^{-30} Cm. [b] Measured at −15 °C. [c] Measured at 25 °C.

The dipole moments of tropothione and tropone were thus determined to be 4.42 ± 0.01 D (in CCl$_4$ at −15.0 °C) and 3.71 ± 0.01 D (in CCl$_4$ at 25.0 °C), respectively, as Table 2 shows. The obtained values indicate that tropothione has the dipolar character *larger* than tropone in the ground state.

Theoretical Considerations.

It is surprising that the dipole moment (μ = 4.42 D) of tropothione (**1**) is larger than that (μ = 3.71 D) of tropone (**2**). Usually, carbonyl compounds have larger moments than thiocarbonyl ones. For example, the dipole moment of acetone (μ = 2.80 D) is larger than that of thioacetone (μ = 2.41 D).[7b]

In order to asses the observed data, ab initio calculations have been carried out, using the GAUSSIAN 92 program.[14] Table 3 shows total energies (E_T's), theoretical dipole moments (μ's), and electronic net charges (ρ's, positive value mean cationic atoms) with various computational methods. In Table 3, dipole moments of tropone by the Hartree–Fock level (RHF/6-31G*// or RHF/6-31G**//) are ca. 20% overestimated relative to μ = 3.71 D (present experimental value). This overestimate has been known well for a variety of molecules.[15] The RHF methods with double-zeta level basis sets overestimate the electron movement in molecules as Table 3 shows. The second-order Møller–Plesset perturbation (MP2) method refines the electron movement. MP2/6-311G*//RHF/6-31G** has given a value 3.758 D close to the observed one, 3.71 D. The 6-311G** basis set matches appropriately the MP2 wavefunction.[16] This result suggests that MP2/6-311G** method gives fairly good electron-movement and reproduces physical properties dependent upon charge distributions. As for net charges, the carbonyl carbon and oxygen atoms are cationic and anionic, respectively, regardless of computational methods.

Table 3. Total Energy (E_T), Dipole Moment (μ) and Charge Density (ρ) of Tropone (**2**).

Method	E_T + 343 (a.u.)	μ (D)	ρ on C(1) [a]	ρ on O [a]
RHF/6-31G*//RHF/6-31G*	−0.39151	4.590	+0.526	−0.585
RHF/6-31G**//RHF/6-31G**	−0.40194	4.582	+0.501	−0.583
RHF/6-311G*//RHF/6-311G*	−0.46017	4.511	+0.442	−0.459
RHF/6-311G**//RHF/6-311G**	−0.46983	4.486	+0.373	−0.453
MP2/6-31G*//RHF/6-31G*	−1.43679	3.973	+0.398	−0.456
MP2/6-31G**//RHF/6-31G**	−1.48388	3.901	+0.373	−0.452
MP2/6-311G*//RHF/6-311G*	−1.57829	3.854	+0.307	−0.325
MP2/6-311G**//RHF/6-311G**	−1.62004	3.758	+0.236	−0.316
experimental [b]		4.30		
experimental [c]		4.17		
experimental [d]		3.71		

[a] Atomic charges on the carbonyl carbon, C(1), and oxygen atoms. [b] Ref. 5. [c] Ref. 6. [d] Present work.

Table 4 shows results of tropothione. Again, the Hartree–Fock calculations give overestimated values of the dipole moment, and the MP2 calculations give better data. The MP2/6-311G**//RHF/6-311G** value 4.568 D is in good agreement with the experimental one, 4.42 D. With all computational methods, the thiocarbonyl carbon atom is anionic, which is opposite to the cationic carbonyl carbon in Table 3.

A question arises out of the present experiment and ab initio calculations. While the electronegativity of the sulfur atom is smaller than that of the oxygen atom, the dipole moment of **1** is larger than that of **2**.

Table 4. Total Energy (E_T), Dipole Moment (μ) and Charge Density (ρ) of Tropothione (**1**).

Method	E_T + 666 (a.u.)	μ (D)	ρ on C(1) [a]	ρ on S [a]
RHF/6-31G*//RHF/6-31G*	–0.03069	5.937	–0.062	–0.236
RHF/6-31G**//RHF/6-31G**	–0.04117	5.924	–0.088	–0.233
RHF/6-311G*//RHF/6-311G*	–0.10083	5.883	–0.153	–0.188
RHF/6-311G**//RHF/6-311G**	–0.11055	5.843	–0.225	–0.180
MP2/6-31G*//RHF/6-31G*	–1.03087	4.827	–0.101	–0.166
MP2/6-31G**//RHF/6-31G**	–1.07811	4.701	–0.128	–0.157
MP2/6-311G*//RHF/6-311G*	–1.16105	4.738	–0.218	–0.090
MP2/6-311G**//RHF/6-311G**	–1.20288	4.568	–0.296	–0.075
experimental [b]		4.42		

[a] Atomic charges on the thiocarbonyl carbon, C(1), and sulfur atoms. [b] Present work.

Fig. 1 exhibits the electronic charges. Tropothione has the zwitter-ionic structure, anionic thiocarbonyl moiety and cationic hexatriene one. This zwitter-ionic structure gives a large dipole moment. On the other hand, tropone cannot reproduce the zwitter-ionic structure because of the anionic carbons (C-2 and C-7) connected to the carbonyl carbon. Accordingly, tropone involves the local dipole moment-vectors opposite to that of the carbonyl bond. The partial cancellation of the dipole moment-vectors leads to the small dipole moment of tropone. This strange trend can be explained by the difference between the $p\pi$-orbital energy levels of the oxygen atom and the sulfur atom. Fig. 2 shows the orbital interactions between the π orbitals of cycloheptatrienyl moiety and the $p\pi$ orbital of a heteroatom. In tropone (**2**), the interaction of $p\pi$ of the oxygen atom with the π_1 and π_2 of the triene is dominant because of the low-lying oxygen $p\pi$ orbital. The charge-transfer interaction from the π_1 to the $p\pi$ weakens the C(1)–C(2), C(1)–C(7), and C(4)–C(5) bonds.

The orbital mixing of the π_1 and π_2 through $p\pi$ is large in the HOMO of **2**.[17] When our attention is focused on the sign of the component orbitals of the HOMO, it is represented approximately as follows:

$$\text{HOMO} = p\pi - \pi_1 + \pi_2$$

This orbital mixing moves the π electron densities from C(1), C(3) and C(6) atoms to C(2), C(4), C(5) and C(7) atoms. This electronic charge movement is shown in the coefficients of the HOMO of tropone in comparison with π_2 of cycloheptatriene moiety. The accumulation of π electron densities on C(4) and C(5) makes the C(4)–C(5) π bond strong. In short, the interaction of $p\pi$ with the π_1 and π_2 weakens the C(1)–C(2) and C(1)–C(7) bonds and diminishes the π electron densities on C(1).

In tropothione, the dominant orbital interaction is between $p\pi$ of the sulfur atom, π_2 and π_3 because of the high-lying sulfur $p\pi$ orbital. The HOMO of tropothione is represented approximately as follows:

$$\text{HOMO} = p\pi + \pi_2 + \pi_3$$

This orbital mixing moves the π-electron densities from C(3), C(4), C(5) and C(6) atoms to C(1), C(2) and C(7) atoms in contrast to the case of tropone. This electron movement is represented in the coefficients of the HOMO of tropothione in Fig. 2. In short, the orbital interaction in tropothione accumulates the π electron densities on C(1).

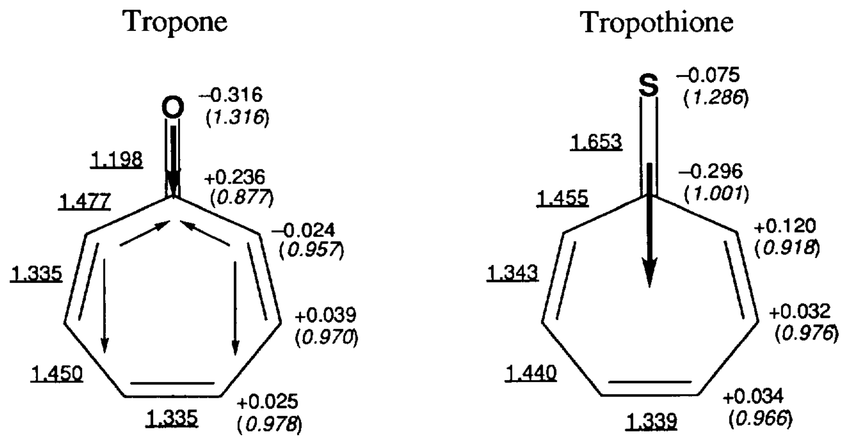


Fig. 1. Geometries optimized with RHF/6-311G** and net electronic charges (positive, cationic) calculated by MP2 density.

In the triene moiety of the ring, the hydrogen net charge is added to the carbon charge. Underlined numbers denote bond distances in Å. Values in parentheses stand for valence π electronic densities. The bold and thin arrows stand for overall dipole-moment vectors and local ones, respectively. It should be noted that tropone has local dipole-moment vectors opposite to that of tropone itself.

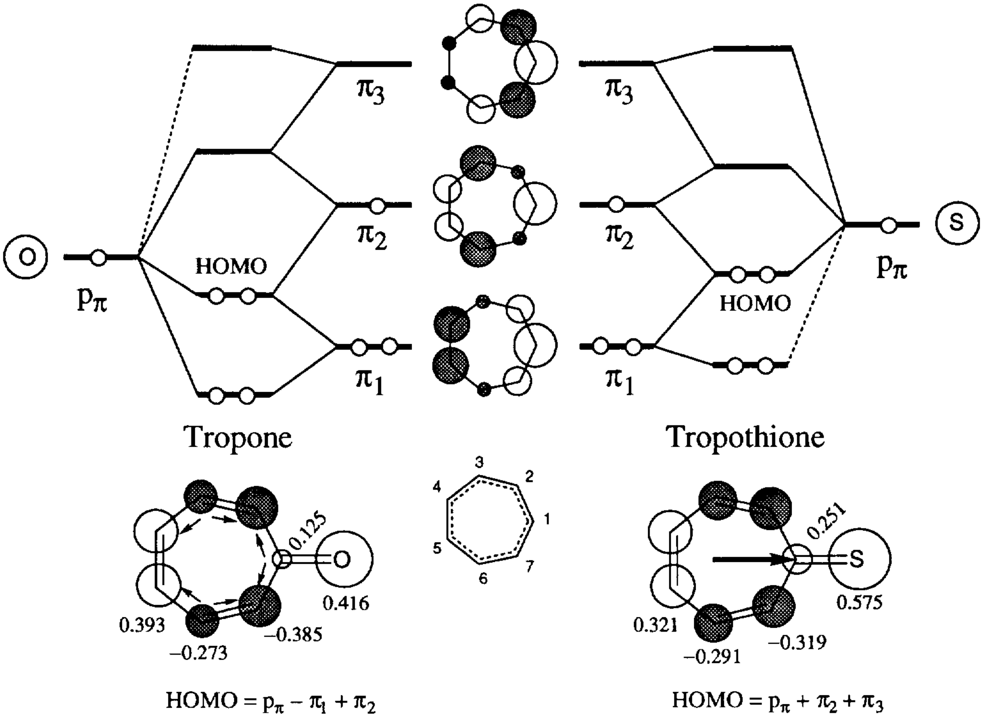


Fig. 2. Orbital interactions between symmetric π orbitals and p_π of the hetero atom.

HOMO coefficients are calculated with the RHF/STO-3G and RHF/STO-3G* methods. The arrows show the movement of π electronic charges through the orbital mixing.

CONCLUDING REMARKS

We have successfully measured the dielectric constants of tropothione (**1**) which is thermally quite unstable. Also, those of tropone (**2**) have been measured. Definite values of dipole moments of two isoelectronic compounds have been obtained.

Old data, 4.30 D[5] and 4.16 D,[6] of tropone which have been standards in nonbenzenoid aromatic chemistry seem to be overestimated. This overestimate would arise from the contamination due to hydration in the tropone sample. The involvement of hydrogen bonds enhances the polarity of molecules generally. In this experiment, the water contamination in the sample has been carefully removed.

The result of μ (tropothione) > μ (tropone) is interpreted in terms of the contribution of charge distribution. The latter molecule suffers from intramolecular cancellation of the local moment vectors. This gives rise to the smaller dipole moment of tropone in Table 5.

Table 5. Summary of the Dipole Moments of Tropothione and Tropone.

	Tropone (**2**)	Tropothione (**1**)
experimental	$\mu = 3.71$ D	$\mu = 4.42$ D
theory[a]	$\mu = 3.758$ D	$\mu = 4.568$ D

[a] Calculated by MP2/6-311G**//RHF/6-311G**

EXPERIMENTAL SECTION

General. The material, tropothione (**1**), was prepared starting from tropone[18] (**2**) and was obtained as pure crystals according to a previously reported method.[8] Tropone was prepared under the conditions without water to prevent a contamination of the hemihydrate according to our previously reported procedure[18] and purified by repeated distillation. The material purities were confirmed by UV–visible spectroscopy as well as the Fourier-transform ^{1}H NMR before and after the dipole moment measurements at a probe temperature of −20 ± 1 °C. The NMR monitoring was carried on a Bruker AM-400 (400 MHz) spectrometer. All the solvents used for the preparation and isolation of tropothione (**1**) were freshly distilled under nitrogen from appropriate drying agents and were all degassed. Spectroscopic grade carbon tetrachloride was used for the dipole-moment measurement. To prevent from the decomposition of **1** in solvent the measurements were performed as rapidly as possible and at low temperature of −15 °C immediately after the isolation of the compound. Isolation experiments for tropothione were performed in a low-temperature-thermostatted room[19] and the material was recrystallized from cold ether to give deep red needles (mp 20–21 °C).

Dipole-Moment Measurement. The electric dipole moment was measured on an instrument[20] (built-in-house) with dilute solutions in spectro grade carbon tetrachloride. The platinum-plated sample cell was equipped with a silicon-oil jacket, and the temperatures were maintained at −15 ± 0.05 °C for **1** and at 25 ± 0.05 °C for **2**. The density (d) measurement was done with an Ostwald–Sprengel pycnometer at six concentrations to obtain an accurate value. The obtained weight fraction, dielectric constant, and density are listed in Table 1. The molar refraction (R_{MD}) for the D sodium line was calculated from values of bond refractions in the literature[21] since it could not be measured directly because of the color of the compound. The electronic polarization is computed from the table of bond refraction; and the atomic polarization was taken as 5% of the electronic polarization. The observed dipole moment includes an inaccuracy of 0.01 D.

Computation. Ab initio MO calculations (STO-3G, STO-3G*, 6-31G*, 6-31G**, 6-311G* and 6-311G**) were carried out by GAUSSIAN 92.[14] All the MO calculations were made on a CONVEX C-3420 computer in the Computer Center of Nara University as well as on a CONVEX C-220 computer in the Information Processing Center of Nara University of Education, Japan.

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