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AN EVALUATION OF THE AROMATICITY IN TROPOTHIONE BASED ON C-13 NUCLEAR MAGNETIC RESONANCE [1)]

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Analyses of the C-13 FT-NMR spectra of tropothione (I) appeared recently as a new troponoid compound and its parent tropone (II) in dilute solutions are reported in order to evaluate the aromatic character in (I). Polyolefinic character of (I) is confirmed and remarkable differences in chemical shifts between (I) and (II) are observed in accordance with the SCF MO calculations.

Tropothione (cycloheptatrienethione) (I) which is 8π electron system, an S-analog of and isoelectronic with tropone (II), seems to be liable to have the same tendency with parent (II) to take a ring π-electron sextet (I').[2)] In our previous paper[3)] we presented the prediction that the dipolar 6π aromatic character (I') of tropothione has been remarkably less than that of tropone[4)], from the semiempirical SCF MO calculations. In order to ascertain the estimated character in (I), we carried out our study on (I) through the analysis of its Fourier transform C-13

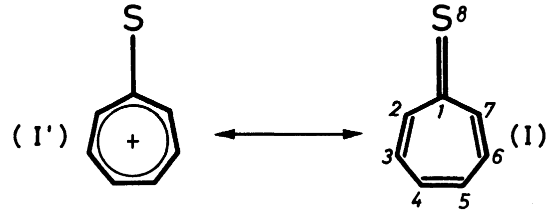
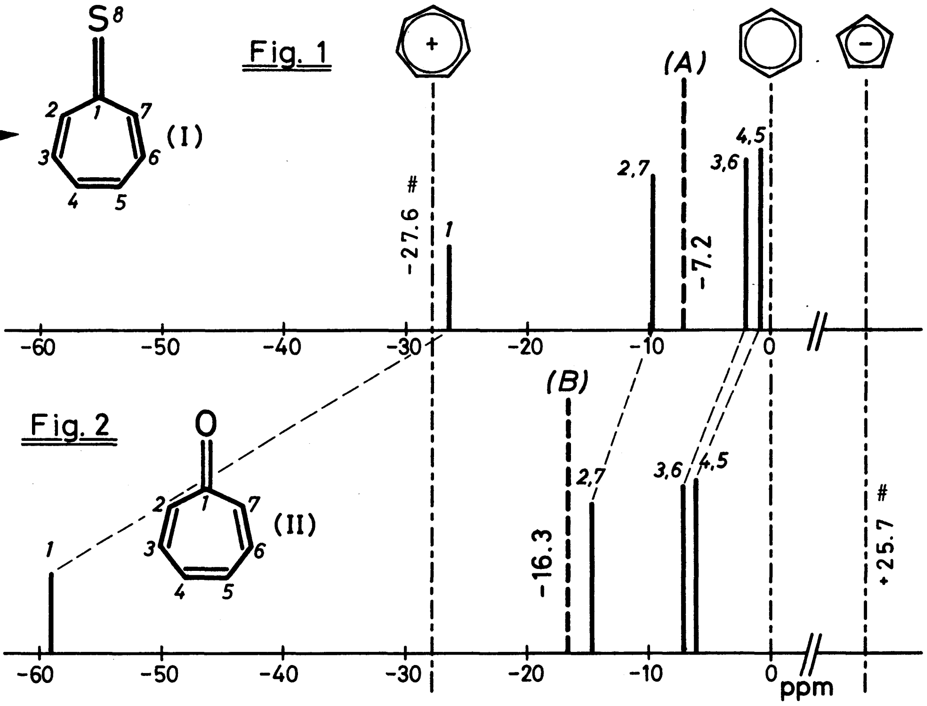


Table 1.

i	$q_\pi(i)$	$\delta_{^{13}C}$ ¶
8	1.307	———
1	0.878	-26.27
2, 7	0.966	-9.59
3, 6	0.965	-1.94
4, 5	0.976	-0.67

¶ ppm from standard benzene

\# see reference 10)



nuclear magnetic resonance. In the preceding SCF MO calculations, the charge densities $q_\pi(i)$ of (I) resulted in the values as shown in Table 1.

A freshly prepared dilute CCl_4 solution of (I) was measured in molar ratio of 0.0177:1, because of its high instability,5) and to make a comparison, the measurement was executed under the same condition as to (II) either.6, 7) The proton noise decoupled C-13 NMR spectrum8) of (I) is shown in Fig. 1, compared with that of (II) in Fig. 2, and the assignments are cited. The shifts are expressed in ppm from the C-13 resonance of benzene. The off resonance technique was used to confirm the thiocarbonyl or carbonyl carbon. The assignments for the individual protonated atoms are based upon the calculated $q_\pi(i)$ of (I)3) and (II)9), with futher inquiring into the enhancement of Nuclear Overhauser Effect. Correlations between the calculated charge densities and the observed shifts $\delta_{^{13}C}(i)$ obtained in both (I) and (II), are visualized in Fig. 3. In comparison with Fig. 1 and 2, particularly on respective weighted mean [dotted line of (A) or (B)], considerable difference in the shifts are observed in accord with the results derived from the SCF MO calculations. We may conclude that this troponoid compound (I) has a typical character of polyolefinic thione rather than aromatic.

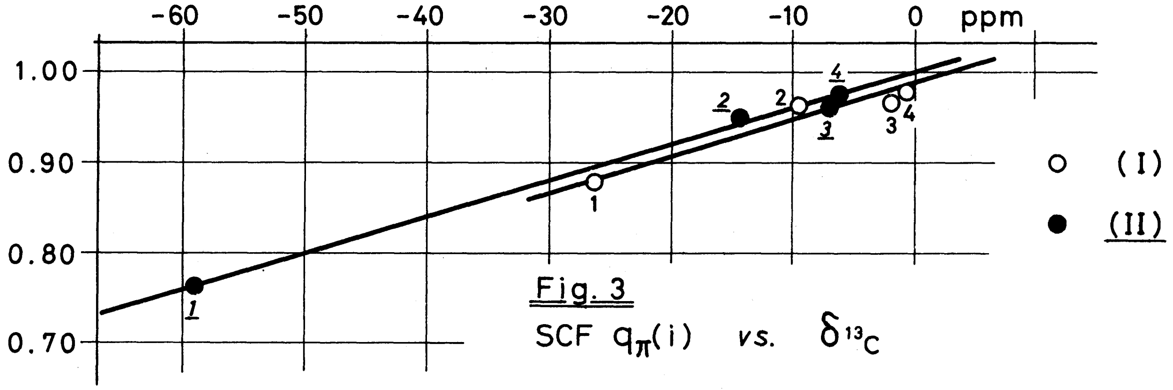


Fig. 3
SCF $q_\pi(i)$ vs. $\delta^{13}C$

REFERENCES AND FOOTNOTES

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5) In a concentrated solution, we find that (I) undergo readily to form several type of spontanious dimerizations; as to this it will be reported in detail in the near future.
6) The C-13 FT-NMR spectra of (I) and (II) have been recorded on a JEOL JMN-PFT-100 spectrometer operating at 25.152 MHz and equipped with a broad band proton decoupler (100 MHz).
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