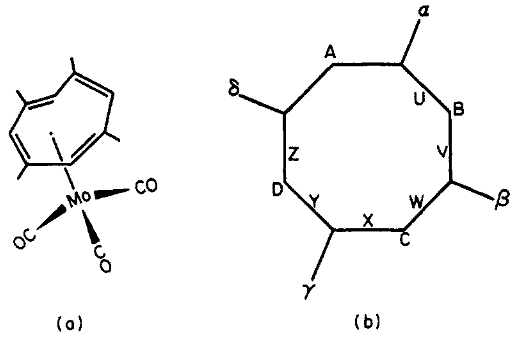


Figure 1. (a) The probable instantaneous molecular configuration. (b) A purely topological diagram (*i.e.*, no bond angles, bond orders, or other structural details implied) of (CH$_3$)$_4$C$_8$H$_4$Mo(CO)$_3$. α, β, γ, δ are the methyl groups. A, B, C, D are the vinyl (ring) protons. U, V, W, X, Y, Z are points at which a perpendicular to the mean ring plane could be erected to coincide with the threefold axis of the Mo(CO)$_3$ group.

The most reasonable assumption[11] for the most favorable or instantaneous molecular configuration would be that shown in Figure 1a; hence the limiting, low-temperature spectrum should consist of four nonequivalent methyl proton resonances and four nonequivalent ring proton resonances. As Figure 2a shows, a spectrum of this type is observed at −30° in DCCl$_3$.[12]

As the temperature is raised, the spectrum undergoes many changes; the behavior is far more complicated than mere collapse of the ring and methyl protons each to a single line. What does happen can be summarized as follows. (1) Two of the vinyl peaks (2,4) and all of the methyl peaks broaden and collapse; the other two vinyl peaks (1,3) show little if any change while this is occurring. (2) In the vinyl region a broad peak begins to appear at a frequency which is the average of those of peaks 2 and 4; simultaneously, a doublet arises in the methyl region, one component at the mean frequency of peaks 5 and 6, the other at the mean frequency of peaks 7 and 8. (3) At still higher temperatures vinyl peaks 1 and 3 broaden and collapse; at the highest temperatures accessible[13] a very broad peak just begins to appear at the mean frequency of 1 and 3. (4) The peak due to averaging of 2 and 4, however, *continues to become sharper* as peaks 1 and 3 are collapsing. (5) As peaks 1 and 3 are collapsing, the methyl doublet begins to broaden and collapse but does not become an unequivocally single peak before decomposition becomes too severe to permit reliable observation.

We propose the following explanation of these facts, using Figure 1b as a purely topological guide. Assume the molybdenum atom to be initially at V. As the temperature rises a V → U → V oscillatory motion (phase 1) commences and accelerates. This averages A with C, α with β, and δ with γ, *viz.*, Scheme I. This explains observations 1 and 2. As the temperature rises further a transannular shift (U → Y → U; V → Z → V) sets in (phase 2), leading to the averaging indicated in Scheme II. This explains results 3, 4, and 5, especially 4.

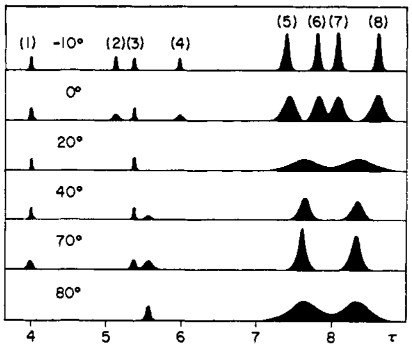
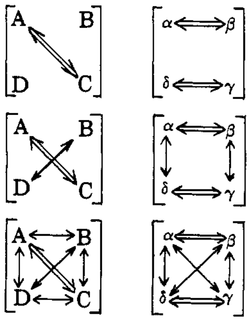


Figure 2. The temperature variation of the proton nmr spectrum of 1,3,5,7-(CH$_3$)$_4$C$_8$H$_4$Mo(CO)$_3$. Temperatures quoted correspond approximately to those for spectra measured on DCCl$_3$ solutions, using a Varian A-60 spectrometer.

The possibility of a cyclic eccentric rotation, U → V → W → X··· → U, which would give Scheme III,



(I)

(II)

(III)

as the second phase, is ruled out within the temperature range of observation by result 4.[14,15]

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[12] The results are qualitatively the same in several solvents, although, of course, slight differences in chemical shifts and small changes in the temperature dependence of line widths are found; full details will be given in a later publication. However, there can be no doubt the phenomena observed are characteristic of the solute molecule itself, with solvent effects being of no essential importance.

[13] (CH$_3$)$_4$C$_8$H$_4$Mo(CO)$_3$ is not very stable thermally; the rate of decomposition becomes appreciable at ~50° and great at temperatures ≥80°. However, allowing for the irreversible production of decomposition products, all the temperature-induced changes in the spectrum are reversible with temperature.

[14] In C$_8$H$_8$Mo(CO)$_3$ the reported single peak at high temperature is consistent with cyclic, eccentric rotation (and also with other possible mechanisms leading to complete averaging). Since in this case there would be no reason why V → W should not occur if U → V occurs, this is entirely reasonable. It then becomes impossible to say whether the transannular or rocking motion plays a role in the C$_8$H$_8$Mo(CO)$_3$ case or not since its effects will be obscured by those of the eccentric rotation. The exact dynamical reason why a V → W shift is appreciably less easy than a U → V or even a Y → Z type shift in 1,3,5,7-(CH$_3$)$_4$C$_8$H$_4$Mo(CO)$_3$ still requires investigation.

[15] We are grateful to the National Science Foundation for financial support.

[16] National Science Foundation Predoctoral Fellow, 1963–1966.

[17] Fellow of the F. Giordani Foundation, Rome, 1965–1966.

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Stereochemically Nonrigid Organometallic Compounds. III. Concerning the Structure of Cyclooctatetraeneiron Tricarbonyl in Solution

Sir:

Since the discovery of cyclooctatetraeneiron tricarbonyl[1-3] and the reports that its proton resonance

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[1] T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 366 (1960).

[2] M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959).

[3] K. Nakamura, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

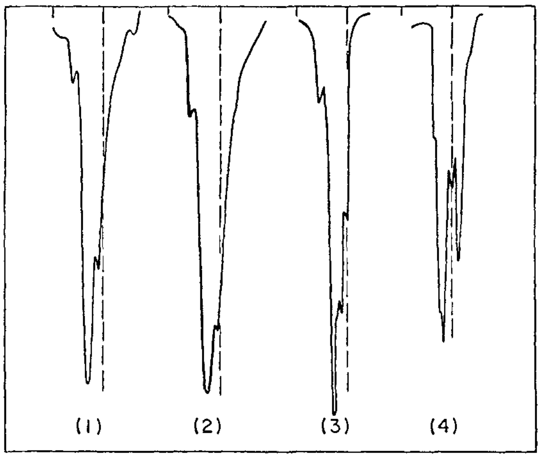

Figure 1. Infrared spectra in the C–H stretching region: (1) $C_8H_8Fe(CO)_3$ in CS_2, (2) $C_8H_8Fe(CO)_3$ in CCl_4, (3) $C_8H_8PtI_2$ in KBr, (4) $C_8H_8Fe(CO)_3$ in crystalline form. The dashed line is at 3000 cm^{-1}.

spectrum consisted of a single sharp resonance, even at[4] −60°, there has been much speculation concerning the nature of this molecule.

An X-ray study[5] showed that the $Fe(CO)_3$ group is associated with four adjacent atoms in the ring (a coordinated 1,3-diene), the other ring atoms forming an uncomplexed 1,3-diene moiety. It has been suggested[5] that the nmr equivalence of the protons is due to a rapid migration of the $Fe(CO)_3$ group among the possible 1,3-diene positions, implying that the structure in solution is the same as in the solid. We present evidence indicating that the structure in solution is different from that in the solid and propose that the C_8H_8 ring is chelated as a 1,5-diene[6] to the metal.

We have studied both the room-temperature infrared and the low-temperature nmr spectra.

The infrared observations cover three regions. (1) The appearance of three CO stretching bands[8] shows that the C_8H_8Fe geometry destroys the inherent C_{3v} symmetry of the $Fe(CO)_3$ group, leaving at best C_s symmetry. (2) The spectrum in the region below 1600 cm^{-1} is too complex to provide any conclusive distinction between 1,3 and 1,5 structures.[11] (3) The C–H stretching region (not reported in detail in ref 10) favors a 1,5 structure. Figure 1 shows that solution spectra of $C_8H_8Fe(CO)_3$ differ markedly in appearance from the solid-state (1,3 structure) spectrum but closely resemble the spectrum of $C_8H_8PtI_2$ (where a 1,5 structure is virtually certain).

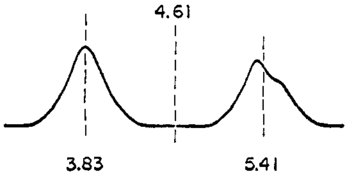

Figure 2. The proton resonance spectrum of $C_8F_8Fe(CO)_3$ in a 1:1 $CHFCl_2$–CF_2Cl_2 mixture at about −155°. Numbers are τ values. The dashed line at τ 4.61 gives the position of the single resonance at room temperature.

We find that $C_8H_8Fe(CO)_3$ has a temperature-dependent nmr spectrum. The single resonance at τ 4.6 first collapses, then disappears ($\sim -100°$). As the temperature is lowered, two new resonances appear and at $\sim -155°$ the spectrum[12] (Figure 2) consists of two broad resonances of equal intensity at τ 3.8 and 5.4.

This spectrum is clearly inconsistent with the "frozen" structure, being of the 1,3-diene type for which we would expect[13] the nonbonded olefin proton resonances close to or less than τ 4.3 with relative intensity 4, the inner protons[14] of the bound diene group at a little higher field ($\tau \sim 4.8$) with relative intensity 2, and the outer protons[14] at appreciably higher fields ($\tau \geq 6$) with relative intensity 2. With incomplete resolution we might have at worst a low-field group with relative intensity 6 and a high-field group with relative intensity 2.

The spectrum is, however, that expected for a tub-bonded (1,5-diene) C_8H_8 group in which the high-field resonance is due to protons (H_1, H_2, H_5, H_6) of the complexed 1,5-diene and the low-field resonance due

[4] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind.* (London), 553 (1961).

[5] B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961); *J. Chem. Phys.*, **37**, 2084 (1962).

[6] There are several examples of iron bonded to chelating nonconjugated dienes, $C_7H_8Fe(CO)_3$, $C_8H_2(CH_3)_4(CF_3)_2Fe(CO)_3$, and $C_8H_{10}FeC_8H_{12}$. The fact that iron carbonyls are known to cause the rearrangement[7] of 1,5- to 1,3-dienes does not necessarily imply that 1,3- are stronger than 1,5-diene–iron bonds. Also from the diolefin $Fe_2(CO)_9$ we have synthesized 1,5-cyclooctadiene–$Fe(CO)_3$ as yellow crystals, mp 61–63°; nmr: τ 6.3 and 7.6 with relative intensities 1:2. The complex does not rearrange in solution to the 1,3-bonded species on standing.

[7] J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

[8] Early reports claimed only two; recently subsequent to the completion of our infrared work,[9] the resolution of three CO stretching bands was also reported.[10]

[9] *Cf.* the article by F. A. Cotton in the Proceedings of the 9th Robert A. Welch Foundation Conference on Chemical Research, "Organometallic Compounds," Nov 15–17, 1965, in press.

[10] R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Am. Chem. Soc.*, **87**, 5346 (1965).

[11] Bailey, Lippincott, and Steele[10] have argued only that the data are *consistent* with a 1,3 structure but did not consider the question of their consistency with a 1,5 structure.

[12] A solvent mixture of $CHFCl_2$ and CF_2Cl_2 was used. A mixture of two Freons was suggested to us by Professor F. A. L. Anet, who has informed us that he and Winstein, *et al.*, have also studied the nmr spectrum of $C_8H_8Fe(CO_3)$ at $\sim -150°$, obtaining similar results, but that they are proposing a different interpretation: C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966).

[13] All nmr data cited for other compounds can be found in the tables of M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965). From the assembled data, the following generalizations can be made. (1) The proton resonances of a 1,3-diene moiety bonded to a metal occur characteristically at higher fields than those in the free ligand. (2) They occur as two distinct sets. The innermost protons (2,3) experience a relatively small upfield shift (*ca.* 0.5–1.0 ppm) while the outermost protons (1,4) are shifted to much higher fields (*ca.* 2.5–3.0 ppm) than those found in the uncomplexed ligands. (3) The spectra of complexes of chelating diolefins such as norbornadiene, cycloocta-1,5-diene, and even cyclooctatetraene which is usually coordinated in the tub conformation (as in $C_8H_8PtI_2$, C_8H_8-CoC_5H_5, $C_8H_8RhC_5H_5$, $[C_8H_8RhCl]_2$, etc.), utilizing a 1,5-diene residue for bonding, are also characteristic. The four protons of the bound olefinic groups occur as one resonance which is shifted to higher fields (usually by ~1.8 ± 0.2 ppm) from their position in the free ligand. (4) In all cases olefinic protons on carbon atoms not involved in bonding to the metal have resonances close to their positions in the free ligand.

[14] We wish to draw attention to results[13] on $C_8H_8(Fe(CO_3))_2$ and $C_8H_8(CoC_5H_5)_2$. The former has two resonances of equal intensities at τ 4.4 and 6.9, showing involvement of two (1,3-diene) iron tricarbonyl fragments. A combination of two (1,5-diene) iron tricarbonyl groups would make all protons equivalent leading to a single peak as is observed for the C_8H_8 moiety in $C_8H_8(CoC_5H_5)_2$ (τ 6.3). Secondly, however, the diiron compound appears to us to offer a particularly good model for what the spectrum of a (1,3-diene) iron tricarbonyl group should exhibit, namely, that the resonances of the inner and outer protons of the bound 1,3-diene should be separated by some 2 ppm. This is entirely in accord with the generalizations given in footnote 13.

to the free olefinic protons (H_2, H_3, H_7, H_8). The fact that the high-field resonance is not a single peak but apparently two overlapping peaks of somewhat different widths can be explained on the assumption that the molecule has only C_s symmetry so that two (say H_1 and H_6) protons of the bound olefin groups are in a slightly different environment from the other two (H_2 and H_5).[15,16]

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[15] No prior example of this form of nonequivalence can be cited since all other known 1,5-diene or tub-bonded C_8H_8 complexes either have molecular symmetry making all four protons on the bonded olefins equivalent (*e.g.*, $C_8H_8Mo(CO)_4$, $[C_8H_8RhCl]_2$), or time-average equivalence would be expected owing to rotation of a π-C_5H_5 ring (*e.g.*, in $C_8H_8Co(\pi\text{-}C_5H_5)$ or $C_8H_8Rh(\pi\text{-}C_5H_5)$).

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[17] National Science Foundation Predoctoral Fellow, 1963–1966.

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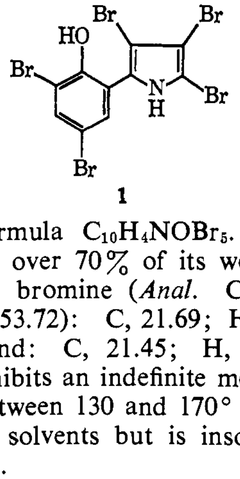
Synthesis of a Bromine-Rich Marine Antibiotic

Sir:

We wish to report the synthesis of an unusual antibiotic (**1**) isolated from a marine bacterium[1] and having



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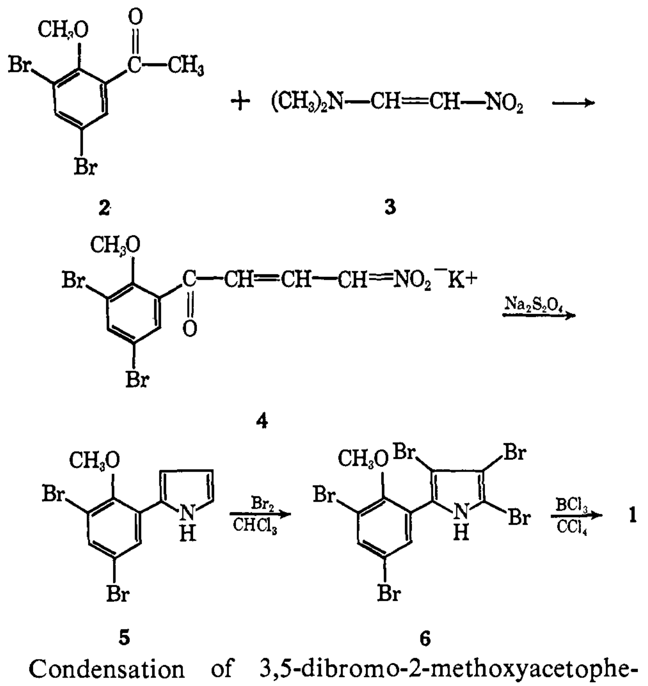
the empirical formula $C_{10}H_4NOBr_5$. The antibiotic is unique in that over 70% of its weight consists of covalently bound bromine (*Anal.* Calcd for $C_{10}H_4NOBr_5$ (mol wt, 553.72): C, 21.69; H, 0.73; N, 2.53; Br, 72.16). Found: C, 21.45; H, 0.73; N, 2.73; Br, 71.23. It exhibits an indefinite melting point with decomposition between 130 and 170° and is soluble in common organic solvents but is insoluble in hydrocarbons and water.

The mass spectrum[2] suggested a molecular weight of 553.5 and the presence of five bromine atoms from the isotope peaks. A preferential and sequential loss of one, two, and three bromine atoms from the molecular ion together with loss of hydrogen cyanide was observed; metastable ion peaks corresponding to these losses were also evident. No fragments corresponding to a simple cleavage of the phenol and pyrrole portions could be seen.

While our studies were in progress, the structure of the antibiotic was established independently by X-ray crystallographic analysis[3] and was kindly communicated to us. The synthesis of this substance was therefore undertaken.



Condensation of 3,5-dibromo-2-methoxyacetophenone[4,5] (**2**) with 1-nitro-2-dimethylaminoethylene[6] (**3**) in the presence of potassium ethoxide and ethanol afforded the intermediate *aci*-nitro salt **4** which was reduced with sodium dithionite essentially according to Severin and Brück[6] to give crystalline 2-(3,5-dibromo-2-methoxyphenyl)pyrrole (**5**), mp 103.5–105°; doublets centered at τ 2.26 and 2.42 (J = 2 cps, aromatic hydrogens) and multiplets centered at τ 3.02, 3.33, 3.62 (pyrrole ring hydrogens), and 6.23 (OCH_3). Bromination of **5** in chloroform at room temperature afforded crystalline 2-(3,5-dibromo-2-methoxyphenyl)-3,4,5-tribromopyrrole (**6**) in good yield, mp 124–125°; doublets centered at τ 2.33 and 2.00 (J = 2.5 cps, aromatic hydrogens), 6.35 (OCH_3). Demethylation of the precursor **6** in benzene or carbon tetrachloride containing a slight excess of aluminum chloride was remarkably fast, some product being formed even within 2 min at 40°. The reaction however was difficult to control as evidenced by the disappearance of both **5** and the product **1** after 5 min and the appearance of by-products of higher mobility on thin layer chromatograms.[7] A satisfactory procedure was found using excess boron trichloride[8] in carbon tetrachloride at room temperature. On standing overnight in the dark the tan solution deposited colorless needles which were presumably a boron chloride complex, since its infrared spectrum showed the lack of a resolved doublet expected of the OH and NH groups in **1**. The complex was decomposed by washing its ethereal solution with dilute hydrochloric acid. Processing the organic phase in the

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[1] The antibiotic was originally isolated by Dr. P. R. Burkholder and co-workers of the Lamont Geological Observatory of Columbia University, Palisades, N. Y., and was kindly provided to us for structure elucidation studies; see P. R. Burkholder, R. M. Pfister, and F. M. Leitz, *Appl. Microbiol.*, **14**, 649 (1966).

[2] We thank Dr. D. C. DeJongh, Chemistry Department, Wayne State University, for recording the mass spectrum and assisting in its interpretation. The spectrum was obtained with an Atlas CH4 mass spectrometer at an ionizing potential of 70 ev and an ionizing current of 18 ma, using a direct inlet introduction system.

[3] F. M. Lovell, preceding paper.

[4] C. M. Christian and G. C. Amin, *J. Indian Chem. Soc.* **36**, 111 (1959).

[5] All compounds reported herein gave correct analyses. Melting points are uncorrected.

[6] T. Severin and B. Brück, *Angew. Chem.*, **76**, 993 (1964); *Chem. Ber.*, **98**, 3847 (1965).

[7] Thin layer chromatography was carried out on silica gel HF plates using the solvent system benzene–2,2,4-trimethylpentane (5:1), and the components were detected under ultraviolet light and by iodine vapor. The antibiotic had an intermediate mobility and produced a rapid and characteristic olive-green color with iodine vapor.

[8] This reagent has been used effectively in demethylation of carbohydrate derivatives: T. G. Bonner, E. J. Bourne, and S. McNally, *J. Chem. Soc.*, 2929 (1960). Aromaic ethers have been demethylated with boron tribromide: J. F. W. McOmie and M. L. Watts, *Chem. Ind.* (London), 1658 (1963).