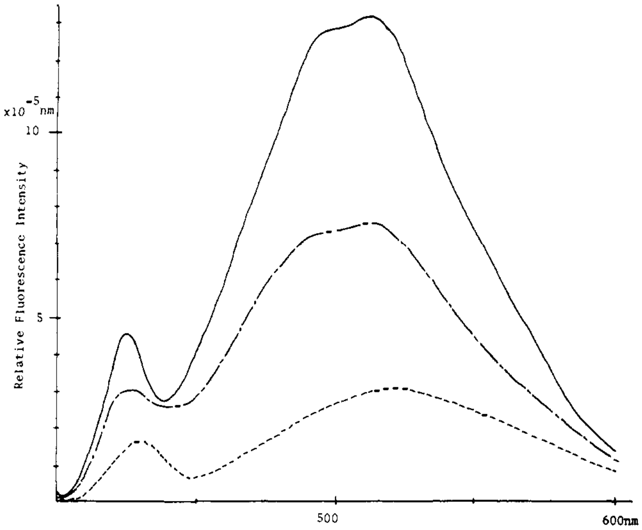

**Figure 1.** Fluorescence spectrum of $0.5 \times 10^{-4}$ M, 1,8-ANS (- - -) on addition of $1 \times 10^{-3}$ M $\beta$-cyclodextrin (– – –) and $1 \times 10^{-3}$ M I (—) at pH 6.98. The exitation wavelength was 375 nm. The fluorescence intensity ($nm^{-1}$) is given so that the quantum yield (quanta emitted/quanta absorbed) was represented by the peak area measured by the wavelength on the horizontal axis (nm).

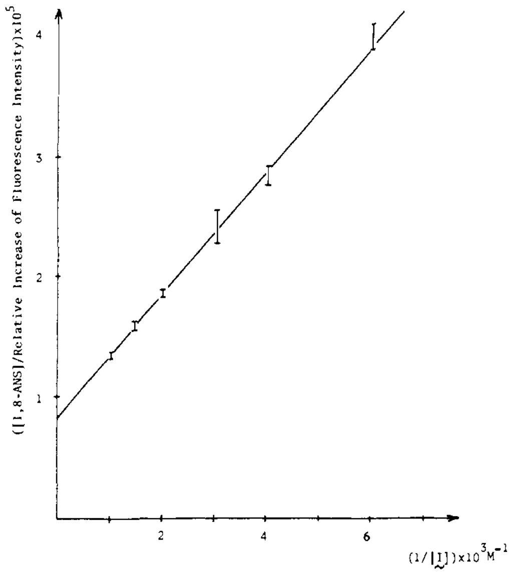

**Figure 2.** The Benesi–Hildebrand plot of 1,8-ANS and I. Error in the figure was calculated by the sum of the error of the mechanical recording noise and dependence of the observed value on the wavelength (between 500 and 540 nm).

45.55; H, 4.58. Calcd: C, 45.39; H, 4.66.

Space-filling models (CPK) of compound I shows it to have an approximately square hydrophobic cavity surrounded by four benzene "walls", the size of the cavity (distance between opposite walls in "face" conformation[4]) being about 7 Å which is large enough to occlude a phenyl or a naphthyl moiety.

An important feature of heterocyclophane I is its solubility in water at pH 7, which introduces a *hydrophobic cavity into the water phase* and facilitated the inclusion of hydrophobic compounds. That this does, indeed, occur was demonstrated through the use of a fluorescent hydrophobic guest, sodium 1-anilino-8-naphthalenesulfonate (1,8-ANS).[5] As shown in Figure 1, there is a strong enhancement in the fluorescence intensity of this compound in the presence of the heterocyclophane I, an enhancement greater than that produced by $\beta$-cyclodextrin.[1b,6] Plotting the fluorescent intensity against the reciprocal of the concentration of I (Benesi–Hildebrand plot[6]) produces a straight line from which the association constant of I and 1,8-ANS can be calculated to be $1.6 \times 10^3$ $M^{-1}$, a value that is 28 times greater than that for $\beta$-cyclodextrin. Experiments are currently under way to test compound I or its derivatives as inclusion catalysts.

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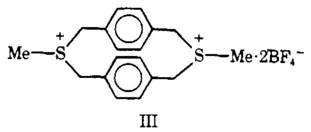
(4) "Face" conformation is concluded to be favored for paracyclophanes based on the NMR study. See ref 3e.

(5) Such fluorescence enhancement often has been observed for 1,8-ANS, when it is bound to enzymes[5a] or cyclodextrin.[1b,5b] (a) D. C. Turner and L. Brand, *Biochemistry*, **7**, 3381 (1968). (b) Only slight enhancement of fluorescence of 1,8-ANS was observed on addition of standard compound, *S,S'*-dimethyl-2,11-disulfonium[3.3]paracyclophane difluoroborate (III).



III

The Benesi–Hildebrand treatment gave $K_{ass}$, which was smaller than 50 $M^{-1}$

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**Iwao Tabushi,* Hideaki Sasaki, Yasuhisa Kuroda**
*Department of Pharmaceutical Chemistry, Kyushu University*
*Fukuoka, 812 Japan*
*Received May 25, 1976*

## Freezing Out the Fluxional Behavior in $Fe(CO)_5$ and Other Metal Carbonyls

*Sir:*

There has been considerable interest over the years in the fluxional behavior of iron pentacarbonyl ($Fe(CO)_5$). While gas phase electron diffraction results[1] show a trigonal bipyramidal geometry, exchange of all CO ligands occurs rapidly on the $^{13}C$ NMR time scale down to the lowest possible solution temperature.[2]

In an elegant study of the $^{13}C$ NMR spectra of *solid* $Fe(CO)_5$, Spiess and co-workers[3] have concluded from both $T_1$ and line-shape measurements that down to at least 100 K $Fe(CO)_5$ is nonrigid, probably via an axial/equatorial exchange mechanism. Below about 100 K $T_1$ becomes extremely long and the difference between the line-shape for a rigid molecule and a slowly exchanging one becomes more difficult to establish. Extrapolation from exchange rates at higher temperatures (213 K, $\tau^{-1} \sim 24$ kHz; 155 K, $\tau^{-1} \sim 13$ kHz; 100 K, $\tau^{-1} \sim 6$ kHz), which allows estimation of an activation energy $\sim$1 kcal $mol^{-1}$, suggests that below about 30 K, the motion will be frozen out.

We have recently prepared a partially oriented sample of $d^6$ chromium pentacarbonyl[4] in solid argon at 20 K, by using polarized visible photolysis. The very fact that this sample did not lose its polarization properties for the duration of the experiment means that the square pyramidal $Cr(CO)_5$ molecule is essentially nonfluxional under these conditions. We have now

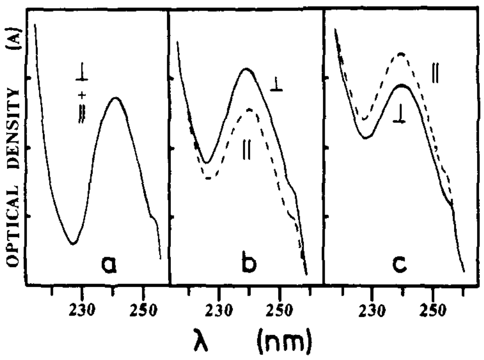

**Figure 1.** Uv band of $Fe(CO)_5$ trapped in a matrix of solid CO at 20 K (ratio 1:500): (a) superimposed spectra with plane polarized light ∥ and ⊥, following deposition from gas phase; (b) spectra after 4.5 h photolysis with λ 255 nm ∥ radiation; (c) spectra after 2 h photolysis with ⊥ radiation.

performed a similar experiment with $d^8$ iron pentacarbonyl and have produced a partially oriented sample of $Fe(CO)_5$ in solid carbon monoxide at 20 K.

Figure 1a shows part of the visible/uv spectrum between 220 and 260 nm of $Fe(CO)_5$ matrix isolated in CO at 20 K (dilution 1:500). Gray and co-workers have assigned[5] the band centered at 240 nm to the transition $^1A_1' \rightarrow {}^1E'$ (i.e., a transition moment of species e′). The gas phase deposited sample is randomly oriented since spectra recorded with light polarized in two perpendicular directions (we label these ∥ and ⊥ for clarity) are superimposable. Similarly, the two ir bands in the "carbonyl stretching" region (of symmetry species e′ and $a_2''$) display constant intensities when recorded in the two different polarizations. Figure 1b shows the same region of the uv spectrum of the sample recorded under identical conditions but after 4.5 h of polarized (∥) photolysis with λ 255 nm (mercury lamp + monochromator + polarizer). The spectral intensity now clearly depends upon polarizer orientation. Figure 1c shows the same spectral region after 2 h photolysis with light of the same wavelength but opposite polarization (⊥). The band intensity behavior is the opposite to that of Figure 1b. Similar polarization effects are seen in the infrared spectrum with the polarization effect ($I_{\parallel}/I_{\perp}$) being in the opposite direction for the two ir bands of different symmetry. The polarization behavior of the uv band at 240 nm during the polarized photolysis mirrors that of the e′ carbonyl stretching vibration, but is opposite to that of the $a_2''$ vibration, thus confirming Gray et al.'s assignment[5] (i.e., transition moment of species e′).

The overall effect of the polarized photolysis is to move the $Fe(CO)_5$ molecules to positions where they have a lower chance of absorbing light of this particular polarization. We discuss possible mechanisms elsewhere[6] but note that in inert matrices (Ar, Xe, $CH_4$ etc.) photolysis of matrix isolated $Fe(CO)_5$ at this wavelength leads to the formation of the $Fe(CO)_4$ fragment. Essentially no $Fe(CO)_4$ is detected in solid CO because of the ready recombination of $Fe(CO)_4$ and CO.[7]

$$Fe(CO)_5 \xrightarrow[CO]{h\nu} Fe(CO)_4 + CO \xrightarrow[\text{recombination}]{} Fe(CO)_5$$

The reorientation step may thus either take place during photolysis, during recombination of $Fe(CO)_4$ with the excess CO, or as an intramolecular rearrangement of $Fe(CO)_4$ itself.

However, knowledge of the exact mechanism is immaterial to the main point. No change in the polarization properties of the system was found during several hours of spectroscopic observation of the sample. If $Fe(CO)_5$ were fluxional under these conditions (i.e., necessitating a continuously changing orientation) maintenance of polarization for more than a fraction of a second would be impossible. We can in fact put an upper limit of $10^{-4}$ $s^{-1}$ on the frequency of any spontaneous process that alters the orientation of $Fe(CO)_5$ matrix isolated in CO at 20 K. Any process which rapidly exchanges ligands and leaves the direction of the figure axis of $Fe(CO)_5$ totally unaffected over several hours would require mutually contradictory properties of the matrix environment; i.e., three of the CO groups are clamped rigidly while the other two CO groups are freely moving. In general, we have no evidence for spontaneous intramolecular rearrangements in binary carbonyls $M(CO)_x$ (M = Fe, Cr) trapped in frozen inert gas matrices. We believe that rearrangements only occur in these systems within a matrix environment when energy is fed into the molecule (as in photolysis[6]). The number, frequency, and relative intensity of the carbonyl ir bands of these molecules allow ready calculation of the angular geometry about the central atom.[8] Asymmetric structures are observed for $Fe(CO)_4$[7] and $Mo(CO)_4$[9] ($C_{2v}$) and $Fe(CO)_3$[10] and $Mo(CO)_3$[9] ($C_{3v}$) and not the more regular structures ($T_d$ and $D_{3h}$, respectively) which would be observed if the suggestion of Sheline and Mahnke[11] that these carbonyls may be fluxional on the infrared timescale was correct.

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**J. K. Burdett, J. M. Grzybowski**
**M. Poliakoff, J. J. Turner***
*Department of Inorganic Chemistry*
*University of Newcastle upon Tyne*
*Newcastle upon Tyne, NE1 7RU, England*

*Received May 24, 1976*

## Synthesis and Structure of a Stable, Crystalline Complex of Methyl Isocyanate

*Sir:*

Whereas complexes of ketenes (**1**)[1] and carbon dioxide (**3**)[2] are now well established, no complex of a simple organic isocyanate has yet been adequately characterized. Complexes of *aroyl* isocyanates have been known for some time[3-5] but the neighboring carbonyl group can participate in the bonding so as to give a five-membered chelate ring (as in **4**) in which the isocyanate function is no longer recognizable. There is good evidence that this is what actually happens[5] and we can reinterpret the experimental results of Collman and his co-workers[3] as being more consistent with structure **4** than with structure **2** (R = ArCO) for the complexes $IrCl(ArCO{\cdot}NCO)(PPh_3)_2$. In particular, we think that it is significant that benzoyl isocyanate displaces dinitrogen from $IrCl(N_2)(PPh_3)_2$ to give **4** (Ar = Ph) but phenyl isocyanate does not.

We now describe the first example of a complex of an organic isocyanate which does not possess potential binding sites apart from those of the isocyanate function. The complex,