

structure II_f or rapidly equilibrating asymmetrical structures III_f are compatible with this result. The effect of cooling gave dramatic evidence in favor of rapidly equilibrating asymmetrical ion structures III_f. The aryl proton peaks lost detail and collapsed into a single broad peak indicating impending non-equivalence of the aryl rings at the lowest temperature it was possible to achieve (-70° in CH_2Cl_2). The corresponding aryl peaks of a model ion (from *p*-anisylcamphenilol)⁵ under the same conditions did not alter significantly.

Chemical Behavior.—Under conditions of complete ionization, symmetrical ion II_f should not undergo rapid aromatic substitution because of the delocalization of positive charge into both aryl rings. Ions III_f would have at any instant only one aryl ring conjugated with the charge; hence, substitution in the non-conjugated ring should be rapid. This latter prediction agrees with the results of semiquantitative experiments, comparing the rates of aromatic substitution of ions from II_f with the behavior of model compounds, by observing the changes in n.m.r. spectra (Table III).

We conclude on the basis of all four experimental criteria that diarylnorbornyl carbonium ions possess rapidly equilibrating asymmetric ion structures III. This result does not rule out the possibility of bridged structures for non-aryl substituted norbornyl or other non-classical carbonium ions, but it stresses the desirability of reopening the question of the structure of such intermediates.³

Acknowledgments.—This work was supported, in part, by a grant from the National Science Foundation (to P. R. S.). We wish to thank Professor Norman C. Deno for his interest, for providing stimulating ideas and discussion, and for experimental assistance.

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RECEIVED OCTOBER 24, 1962

THE MOLECULAR AND CRYSTAL STRUCTURES OF π -CYCLOPENTADIENYL π -CYCLOHEPTATRIENYL VANADIUM

Sir:

The compound $(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)\text{V}$ was prepared by King and Stone,¹ who proved the compositions and showed that the compound was paramagnetic with one unpaired electron per molecule. They named the compound π -cyclopentadienyl π -cycloheptatrienyl vanadium, proposing a structure with the vanadium atom "sandwiched" between five- and seven-membered rings.

Structures of π -cycloheptatrienyl metal complexes have not previously been reported, and reservations as to their existence have been raised.² We report here complete confirmation of the sandwich structure for $(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)\text{V}$, and the first structural information on a π -cycloheptatrienyl compound.

Crystals of the compound are orthorhombic with space group Pnma; lattice constants $a = 11.058 \pm 0.014 \text{ \AA}$, $b = 10.845 \pm 0.016 \text{ \AA}$, $c = 7.929 \pm 0.007 \text{ \AA}$, determined from back reflection Weissenberg diffraction patterns, require four molecules per unit cell.

Intensity data were collected on a General Electric single crystal orienter using a theta-two theta scan

(1) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 5263 (1959).

(2) H. P. Fritz and R. Schneider, *Ber.*, **93**, 1171 (1960).

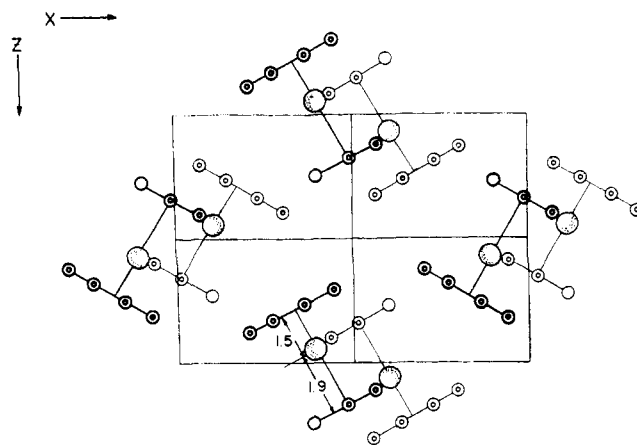


Fig. 1.—Projection onto (010). Heavy lines are molecules at $y = 3/4$, light lines are molecules at $y = 1/4$.

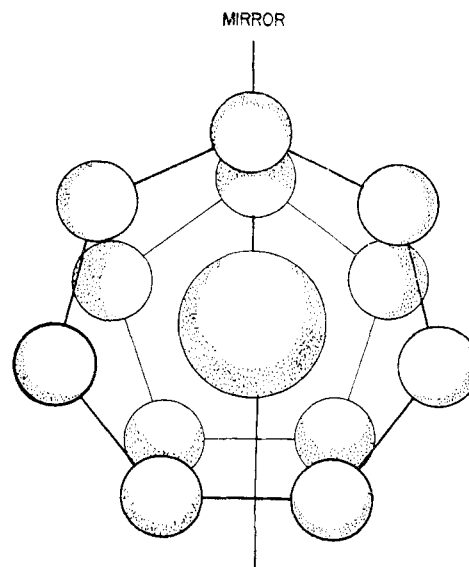


Fig. 2.—Projection of molecule perpendicular to the molecular axes.

technique. A three dimensional Patterson map led to vanadium atom coordinates $x/a = 0.144$, $y/b = 0.25$, $z/c = 0.464$ in $4c$ of Pnma, so that the molecules possess mirror symmetry. A complete but not thoroughly refined structure has been found.

The vanadium atom lies between C_5 and C_7 rings (Fig. 1 and 2); the rings are bisected by mirror planes so that one apex carbon atom of each ring lies on a mirror plane as shown in Fig. 2.

The perpendicular distance from the vanadium atom to the C_7 ring is 1.50 \AA , while the distance to the C_5 ring is 1.90 \AA . The V-C (7-ring) distances are 2.25 \AA , while the V-C (5-ring) distances are 2.23 \AA , equal within the limits of our current stage of refinement. It appears, then, that V-C distances are the main factor controlling the distance of vanadium to the two rings. The C-C distances are 1.403 \AA in the C_7 ring and 1.424 \AA in the C_5 ring. Both rings are symmetrical within our present accuracy. The bonding here is not to be likened to that in $\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$ ³; in cycloheptatriene complexes the presence of a methylene carbon prevents equivalence of the ring carbons.

The present discrepancy factor, R , is 0.186 for 969 observed reflections; for the $\{hk0\}$ data only $R = 9.6\%$.

At this stage of refinement it appears that the torsional amplitudes of the rings about their common axis

(3) J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, **43**, 2188 (1960).

are less than in any of the corresponding cyclopentadienyl complexes.

The short perpendicular distance of the cycloheptatrienyl ring from the metal atom suggests that π -dicycloheptatrienyl-metal compounds would have carbon-carbon inter-ring contacts of about 3.1 Å. even if the two rings were staggered, resulting in considerable steric resistance to the formation of such compounds as, for example $(C_7H_7)_2Ti$ (effective atomic number = 36).

The authors are most grateful to Prof. F. G. A. Stone for calling their attention to this problem, and for supplying crystals for the X-ray study.

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WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S.
ATOMIC ENERGY COMMISSION. CONTRIBUTION No. 1261.

RECEIVED JANUARY 7, 1963

STEREISOMERIC TRIPLET STATES OF AN α -DIKETONE¹ Sir:

In the accompanying communication¹ we have described chemical evidence from which we inferred that the lowest triplet states of conjugated dienes may exist in relatively stable *cis* and *trans* isomeric modifications. Since phosphorescence from diene triplets cannot be detected, at least one of the common means for characterization of triplet states cannot be used to shed further light on the problem. However, we might reasonably expect that there should be similar isomeric modifications of the lowest triplet states of α -diketones.

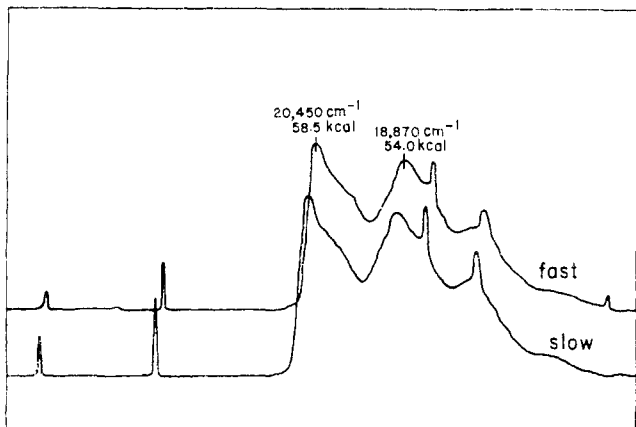


Fig. 1.—Phosphorescence spectrum of β -naphthil in EPA. Results with fast and slow chopping rates are shown. Sharp lines are scattered light from the source.

We have for some time been perplexed by curious features of the phosphorescence spectra of several α -diketones.² For example, the phosphorescence spectrum of benzil in an ether (5 parts)-isopentane (5 parts)-ethanol (2 parts) (EPA) glass at 77°K. is a broad band with a maximum at 20,040 cm^{-1} and a weak shoulder at about 21,200 cm^{-1} .³ However, we find that in a glass prepared from methylcyclohexane (5 parts) and isopentane (1 part) (MCIP) the phosphorescence spectrum shows two well resolved maxima

(1) Mechanisms of Photoreactions in Solution XIV. Part XIII is G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963).

(2) All spectra were taken at 77°K. on Kodak spectroscopic plates by means of a quartz prism spectrograph. Microdensitometer tracings, as shown in Fig. 1, 2, and 3, were recorded directly from the spectroscopic plates. A mercury lamp was used as the incident light source and mercury emission lines (the sharp peaks in the spectra) were used for calibration.

(3) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944), reported the 0-0 phosphorescence band of benzil in EPA at 90°K. to be at 21,600 cm^{-1} .

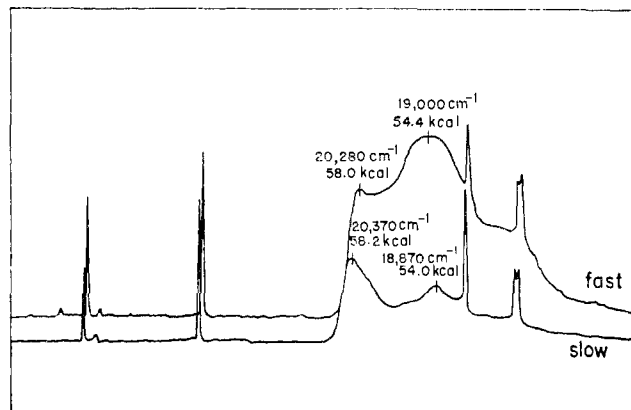


Fig. 2.—Phosphorescence spectrum of β -naphthil in MCIP. Results with fast and slow chopping rates are shown.

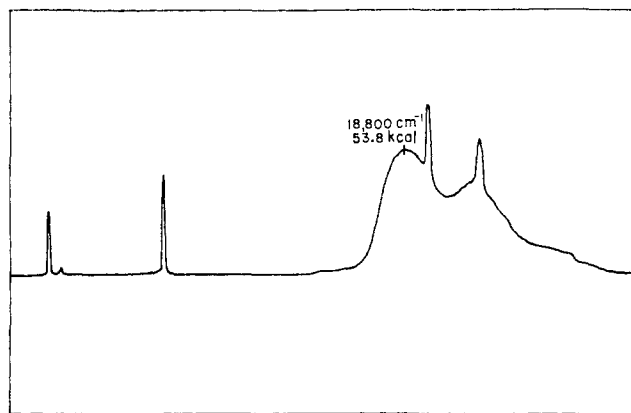
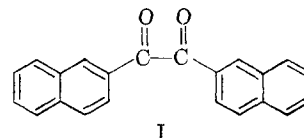


Fig. 3.—Phosphorescence spectrum of β -naphthil in isopentane-3-methylpentane.

at 18,800 and 17,240 cm^{-1} . While we have observed shifts in the phosphorescence spectra of many compounds as the solvent is changed from EPA to MCIP, the apparent shift for benzil is much larger than normal.

The spectrum of β -naphthil (I) in EPA shows clear resolution of three maxima at 20,450, 18,870 and 17,390



cm^{-1} (Fig. 1). The spectrum in MCIP (Fig. 2) also shows three slightly shifted maxima at 20,280, 19,000, and 17,400 cm^{-1} . However, the relative intensities of these bands do not correspond with those observed in EPA. Since a rotating sector was used to separate fluorescence from phosphorescence, it was very easy to change the delay time between excitation and measurement of the emission. As shown in Fig. 1 the rate of rotation of the sector does not affect the spectrum obtained in EPA. However, the relative intensities of the maxima in the MCIP spectrum change drastically when the rate of rotation of the sector is varied. Furthermore, the spectrum obtained in MCIP using a slow sector speed (Fig. 2) is remarkably similar to the spectrum obtained in EPA. It shows maxima at 20,370, 18,870, and 17,330 cm^{-1} . This result seems to indicate quite unequivocally that the emission in MCIP arises from two different triplets having different radiative lifetimes. Control experiments showed that none of the emission arises from the solvent.

While other explanations probably could be advanced to account for the results, we are strongly inclined toward the view that the two emitting species are *cis* and *trans* isomeric triplets of the diketone. Consequently