Table I. Analytical Results

		% C	% H	% N	% Cl	% Pt
H^+	Calcd	37.10	2.84	7.23	27.50	25.00
$[C_6H_5N{=}NC_6H_5]_2PtCl_6^{2-}$	Found	36.47	2.89	7.26	28.38	25.20
H^+	Calcd	32.50	2.50	6.30		
$[C_6H_5N{=}NC_6H_5]_2HgBr_4^{2-}$	Found	32.05	2.60	6.11		
		31.70	2.52	. . .		
H^+	Calcd	50.90	3.89	9.90		
$[C_6H_5N{=}NC_6H_5]ClO_4^-$	Found	50.71	3.97	10.14		

Further evidence that the compound was a salt was obtained from a comparison of its ir spectrum with the spectra of other azobenzene salts. $[AB{-}H^+]ClO_4^-$ was prepared by the method of Jaffé.[7] (We find that this compound is not hygroscopic, although it has been described as such.[7]) The perchlorate can also be prepared by mixing together acetic acid solutions of 70% $HClO_4$ and azobenzene. Acetic acid appears to be a good solvent for preparing the conjugate acid salts of azobenzene. $[AB{-}H^+]_2HgBr_4^{2-}$ was prepared by bubbling anhydrous HBr through a mixture of 0.5 g of $HgBr_2$ and 10 ml of glacial acetic acid until all the $HgBr_2$ had dissolved followed by the addition of 1.0 g of azobenzene in 20 ml of glacial acetic acid. The precipitate which formed immediately was filtered and washed repeatedly with glacial acetic acid and then with dry hexane. Analytical results are collected in Table I.

The infrared spectra of all the azobenzene conjugate acid salts are very similar but are different from the spectrum of azobenzene. Figure 1 shows the region above 2500 cm^{-1}, containing the N–H stretch and aromatic C–H stretch vibrations, and the region 1200–1600 cm^{-1}. These were obtained in dry hexachlorobutadiene and Nujol mulls. The ir band at 1390 cm^{-1} in the salts is absent in free azobenzene and is assigned to the N=N stretch. The presence of this band is expected from the asymmetry introduced by protonation. The Raman spectrum of solid azobenzene shows a strong polarized band at 1440 cm^{-1}, but in $[AB{-}H^+]ClO_4$ this band is absent and a strong new band is found at 1407 cm^{-1}. Large relative intensity changes also occur in three of the typical aromatic ring breathing modes at 1580, 1480, and 1450 cm^{-1}. The strong band at 690 cm^{-1} in azobenzene is shifted to 670–675 cm^{-1} in the salts and is a useful indicator for the presence of free azobenzene resulting from partial hydrolysis.

In contrast to our results, Jaffé observed that the ir spectrum in KBr disks of azobenzene and its perchlorate salt were very similar. We find that the spectra of all the salts in KBr disks show the presence of free azobenzene, which may be liberated either by hydrolysis due to traces of water always present in KBr disks, or by interaction with Br^-. These possibilities are suggested by our observations that (a) wet organic solvents cause hydrolysis and (b) the compound $[AB{-}H^+]Br^-$ is unstable with respect to azobenzene and HBr in dry air at room temperature.

The yield of $[AB{-}H^+]_2PtCl_6^{2-}$ shows that 50% of the platinum is consumed by formation of the salt. Since $PtCl_4$ is the only source of chloride ion, the yield cannot exceed 66%. If the filtrate from the reaction is evaporated to dryness and the residue washed repeatedly with dry hexane, a dark brown solid is obtained which contains platinum, azobenzene, and acetate. This compound has not been fully characterized.

We conclude that the compound formulated by Kharasch and Ashford as $[azobenzene]_2PtCl_4$ is in fact $[azobenzene{-}H^+]_2PtCl_6^{2-}$, a salt with no coordination of the azobenzene to platinum. The infrared spectrum of azobenzene is quite different from that of its conjugate acid, and the similarity reported by Jaffé was probably due to decomposition in the KBr disks.

The coordination compounds of azobenzene include an $SbCl_5$ adduct[8] and some uncharacterized silver and copper complexes.[4] The present work indicates that there is, as yet, no evidence for π-olefinic type bonding of azobenzene.

Acknowledgment. We thank the National Science Foundation Grant (GP-6850) for support of this research.

R. G. Denning, J. Thatcher
William Albert Noyes Laboratory
University of Illinois, Urbana, Illinois
Received July 22, 1968

---

[7] S.-J. Yeh and H. H. Jaffé, *J. Org. Chem.*, **24**, 717 (1959).

[8] V. Grutmann and A. Steininger, *Monatsh. Chem.*, **96**, 1175 (1965).

Flash Photolysis of 5-Diazo-10,11-dihydrodibenzo[*a,d*]cycloheptenylidene

Sir:

Recent studies on the optical spectroscopy[1-4] and electron spin resonance (esr)[5-8] of a number of aromatic methylene intermediates have revealed the molecular structure of carbenes to a considerable extent. It is doubtful, however, that one is entitled to discuss the reactivity of carbenes produced at room temperature in connection with the information obtained at 77°K by optical spectroscopy and esr studies. Furthermore, although there have been reported several electronic spectra of methylene[9] and halomethylenes[10] by the flash

---

[1] (a) A. M. Trozzolo and W. A. Gibbons, *J. Am. Chem. Soc.*, **89**, 293 (1967); (b) W. A. Gibbons and A. M. Trozzolo, *ibid.*, **88**, 172 (1966).

[2] I. Moritani, S. Murahashi, M. Nishino, K. Kimura, and H. Tsubomura, *Tetrahedron Letters*, 1373 (1966).

[3] G. L. Closs, C. A. Hutchison, Jr., and B. Kohler, *J. Chem. Phys.*, **44**, 413 (1966).

[4] (a) D. E. Milligan and M. E. Jacox, *ibid.*, **44**, 2850 (1966); (b) C. B. More and G. C. Pimentel, *ibid.*, **41**, 3504 (1964).

[5] R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962).

[6] R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962).

[7] I. Moritani, S. Murahashi, M. Nishino, Y. Yamamoto, K. Itoh, and N. Mataga, *J. Am. Chem. Soc.*, **89**, 1259 (1967).

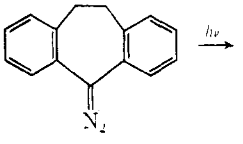
[8] R. A. Bernheim, R. J. Kemph, P. W. Humer, and P. S. Skell, *J. Chem. Phys.*, **41**, 1156 (1964).

photolysis, all of them were obtained in the gas phase.

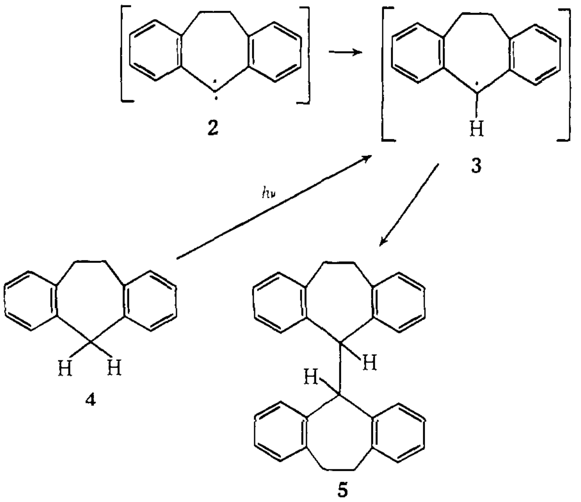
We wish to report here that we have obtained, for the first time, the electronic absorption spectrum of 10,11-dihydrodibenzo[*a,d*]cycloheptenylidene (**2**) by the flash photolysis of 5-diazo-10,11-dihydrodibenzo[*a,d*]-cycloheptadiene (**1**)[11] *in liquid paraffin at room temperature.*

The flash photolysis of a *ca.* 5.3 × 10^{-5} *M* solution of **1** in deoxygenated paraffin at room temperature was studied using the apparatus previously described.[12] The change in the transient spectra was investigated with various delay times in the range from 1 μsec to 1 sec. The absorption spectrum appearing at the delay time of 5 μsec is shown by curve C in Figure 1. The spectrum of the intermediate changed with time and took the shape as shown by curve D at the delay time of 450 μsec, and then disappeared within 25 msec. The lifetime of the former intermediate is estimated to be in the range of about 1–50 μsec.

The spectral feature of curve C agrees well with the spectrum of carbene **2** previously observed in the rigid media at 77°K (curve A), and therefore it may be reasonable to conclude that the same carbene is formed in the liquid paraffin by the flash photolysis. The spectral characteristics of curve D are very similar to those obtained by the flash photolysis of the solution of 10,11-dihydrodibenzo[*a,d*]cycloheptene (**4**) and the photolysis product of **4** in rigid media (curve B) and therefore may safely be assigned to the radical **3**.[13]



1



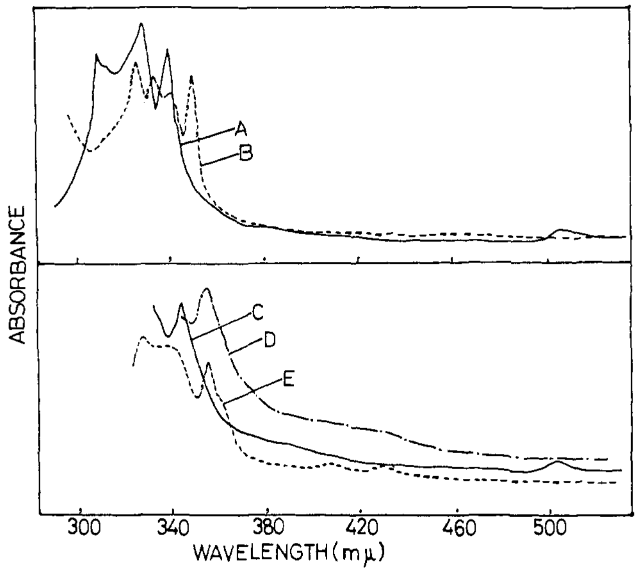


Figure 1. Electronic absorption spectra of 10,11-dihydrodibenzo-[*a,d*]cycloheptenylidene and 10,11-dihydrodibenzo[*a,d*]cycloheptenyl radical: (A) absorption spectrum of carbene **2** produced by photolysis of **1** at 77°K with a Hg lamp; (B) absorption spectrum of radical **3** produced by photolysis of **4** at 77°K with a Hg lamp; (C) absorption spectrum of carbene **2** produced by flash photolysis of **1** at 20° at the delay time of 5 μsec; (D) the same as (C) taken at the delay time of 450 μsec; (E) absorption spectrum of radical **3** produced by flash photolysis of **4** at 20°.

From these results, it seems reasonable to conclude that radical **3** is formed as a result of the hydrogen abstraction by the carbene **2** from the solvent. Analysis of the ultimate products has established that the principal product is 5,5′-bi(10,11-dihydrodibenzo[*a,d*]cycloheptenyl) (**5**) presumably formed by the dimerization of radical **3**. The absorption spectrum of **5** is of course quite different from the transient spectra obtained. When the flash photolysis was carried out in a liquid paraffin solution containing oxygen, spectrum C did not appear and a new transient spectrum with a maximum at 450 mμ was obtained.

In view of the fact that the T–T′ absorption spectrum of carbene **2** can be observed in solution at room temperature at the delay time of 3 μsec, it seems reasonable to assume that the singlet–triplet intersystem crossing may occur within *ca.* 1 μsec at room temperature.

(9) G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959); G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961); G. Herzberg, *Can. J. Phys.*, **39**, 511 (1961).

(10) (a) P. Venkateswarlu, *Phys. Rev.*, **77**, 79, 676 (1950); P. K. Laird, E. B. Andrews, and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950); D. E. Mann and B. A. Thrush, *J. Chem. Phys.*, **33**, 1732 (1960); B. A. Thrush and J. J. Zwolenik, *Trans. Faraday Soc.*, **59**, 582 (1963); R. E. Milligan, D. E. Mann, M. E. Jusk, and R. A. Mitsch, *J. Chem. Phys.*, **41**, 1199 (1964); J. P. Simons, *J. Chem. Soc.*, 5406 (1965); (b) A. J. Merer and D. N. Travis, *Can. J. Phys.*, **39**, 511 (1961); (c) A. J. Merer and D. N. Travis, *ibid.*, **44**, 1541 (1966); (d) *ibid.*, **44**, 525 (1966).

(11) I. Moritani, S. Murahashi, K. Yoshinaga, and H. Ashitaka, *Bull. Chem. Soc. Japan*, **40**, 1506 (1967).

(12) N. Yamamoto, Y. Nakato, and H. Tsubomura, *ibid.*, **39**, 2603 (1966).

(13) The slight differences in the wavelengths of the absorption maxima, and the broadness of the bands, *e.g.*, between A and C in Figure 1, may be attributed to the differences in temperature and solvents. Although there are some other minute disagreements in the spectra of these unstable species, we have reached the conclusion given above in view of the general characteristics of these spectra.

Ichiro Moritani, Shun-Ichi Murahashi, Hidetomo Ashitaka
Katsumi Kimura, Hiroshi Tsubomura
Department of Chemistry, Faculty of Engineering Science
Osaka University, Machikaneyama, Toyonaka, Osaka, Japan
Received July 3, 1968

Deuterium Isotope Effect in Triplet Electronic Energy Transfer Rates. From Benzene and Acetone to Olefins

Sir:

We wish to report a preliminary account of a study of the deuterium rate isotope effect observed in the triplet excitation energy transfer process in the gas