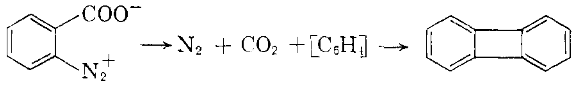
COMMUNICATIONS TO THE EDITOR

SPECTROSCOPIC EVIDENCE FOR GASEOUS BENZYNE

Sir:

We wish to report detection of a volatile precursor of biphenylene from flash photolysis of benzenediazonium-2-carboxylate (I).[1] The short-lived intermediate is tentatively identified as benzyne. This assignment follows a consideration of the source of the species, its ultraviolet spectrum, and the rapidity with which it forms gaseous biphenylene (III). It owes its credibility to the previous accumulation of evidence[2] that such an intermediate is involved in certain aromatic substitution reactions, and in the formation of biphenylene and triphenylene from monocyclic materials.



I II III

Films of solid salt (I) were deposited in a transparent silica tube (60 cm. long, 1.6 cm. diam.) which was evacuated and closed off. Samples were subjected to photolysis by light from a discharge through a silica tube filled with 2–6 cm. of argon. The photolytic flash discharged 750 joules in approximately 20 μsec.; 60 μf. capacitance charged to 5 kv. supplied the energy. When relatively large samples were photolyzed (0.1–0.2 mmole), one could see that immediately following photolysis the tube was filled with a cloud of fine yellow dust which settled in about a minute. Quantities of carbon dioxide and nitrogen produced indicated that approximately 50% reaction occurred under these conditions. The yellow ether extract of the product was separated from considerable insoluble material which was not examined further. Chromatography of the soluble material on alumina with benzene–petroleum ether (30–60°) as eluent furnished biphenylene (m.p. 112–113° after sublimation) and triphenylene (m.p. 198–199°), which were identified by their characteristic ultraviolet spectra in ethanol, in a ratio of approximately 6:1.

Light from a quartz capillary (190 joules in *ca.* 20 μsec.) was passed the length of the sample tube, into a Hilger medium quartz spectrograph. The spectral flash was triggered by the output of a variable delay circuit. In spectroscopic experiments, small samples (0.4 to 20 μmoles) were used and no precipitation was visible.

Spectra taken 5 sec. or more after photolysis indicated biphenylene only, when compared with the spectrum of a gaseous sample prepared from crystalline biphenylene. A delay of 1 msec. likewise revealed only biphenylene, but the intensity of the bands in both the 240 and 350 mμ regions indicated that its pressure was considerably above the equilibrium vapor pressure. Spectra taken 200 μsec. after initiation of photolysis revealed biphenylene long-wave-length bands, in addition to intense absorption in the region below 270 mμ by a species apparently different from biphenylene. At 10 μsec., with relatively large samples (20 μ moles), the long-wave-length bands of biphenylene were barely detectable, yet the region below 270 mμ was virtually opaque and strong absorption extended beyond 300 mμ. Use of smaller samples allowed a study of the spectrum of the intermediate 10 μsec. after initiation of photolysis.

The spectrum of the intermediate divides itself into several regions: (1) very weak absorption at wave lengths greater than 270 mμ; (2) slightly stronger absorption from 270 to about 255 or 250 mμ; (3) distinctly stronger absorption in the region 250–235 mμ, and (4) very strong absorption beyond 230 mμ. Thus far, our efforts have been directed principally at studying the 250–235 mμ region. We find a broad maximum between 238.5 and 241.5 mμ. Table I gives plate densities for comparison flash and photolyzed sample, as well as raw differences and differences multiplied by scale factors to correct for plate response, for a typical experiment. It is difficult to estimate the extinction coefficient at λ_{max} because instantaneous concentrations are not known. A minimum value can be set, however, at about 600.

TABLE I

DENSITOMETER READINGS OF PLATE DENSITY IN THE 240 Mμ REGION

λ, mμ	Plate Density			
	Photolysis	Blank	Difference	Corrected[a]
249.6	0.460	0.520	+0.060	+0.060
245.6	.309	.439	.130	.135
243.3	.197	.340	.143	.165
241.9	.180	.335	.155	.185
241.2	.160	.320	.160	.200
240.4	.154	.314	.160	.197
239.8	.147	.295	.148	.190
239.1	.138	.276	.138	.184
238.4	.146	.265	.119	.168
237.7	.143	.255	.112	.162
237.0	.148	.253	.105	.161
234.8	.152	.245	.093	.146
231.3	.123	.155	.032	.083

[a] Difference corrected for plate response; spectrum taken on Ilford Zenith plate; delay of 10.8 μsec.

Since the broad absorption maximum of the intermediate is so near the much sharper peak of gaseous biphenylene at 237.5 mμ, we should entertain the possibility that the transient spectrum is due to excited biphenylene. At times 1 msec. or less after photolysis, the stronger long-wave-length band of biphenylene appears broad, with λ_{max} at 358.7 mμ. After two minutes, this band seems narrower, and λ_{max} shifts to 354.3 mμ. This

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[1] M. Stiles and R. G. Miller, THIS JOURNAL, **82**, 3802 (1960).

[2] See G. Wittig, *Angew. Chem.*, **69**, 245 (1957); J. D. Roberts, Chemical Society (London) Special Publication No. **12**, 115 (1958); R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

seems to indicate that biphenylene is formed in vibrationally-excited states. Nonetheless, persistence of the absorption maximum at about 240 mμ for times up to 200 μsec., together with the fact that the long-wave-length bands of biphenylene are exceedingly weak at times when absorption in regions (1) and (2) is quite strong, indicates to us that the transient spectrum is not from excited biphenylene.

Drawing an analogy with the pyridine spectrum, one can make a speculative assignment of bands consistent with the benzyne structure. Regions (1) and (2) would be assigned to n → π* excitation, the band being broad (rather than sharp as in pyridine) because such a transition in benzyne would be accompanied by a large change in equilibrium nuclear configuration. Absorption in the 240 mμ region could be assigned to a π → π* transition, like that of pyridine in the 245–270 region.

Further work will be directed principally toward studying other spectral regions more closely and obtaining a detailed theoretical interpretation of the structure and spectrum of the transient intermediate.

We are grateful to Mr. Roy G. Miller for preparing the benzenediazonium-2-carboxylate, and to Mr. Wayne G. Warren for his part in constructing the apparatus. This work was supported in part by a contract with the United States Air Force Office of Scientific Research.

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THE STABILITY OF INTERPEPTIDE HYDROGEN BONDS IN AQUEOUS SOLUTION

Sir:

X-ray diffraction and infrared spectra provide direct evidence for interpeptide hydrogen bonds[1] for substances (model peptides or proteins) in the solid state where the bond strength is high. In aqueous solution, however, where water provides competing groups, the stabilizing effect of such bonds is much more uncertain. The intrinsic stability of the N–H·O=C bond in water actually never has been measured despite the fact that it is a fundamental quantity in any analysis of the configuration of proteins in aqueous solution. An attempt to estimate its free energy of formation was made by Schellman,[2] based on an analysis of literature data for the thermodynamic behavior of urea solutions, but this computation is based on the risky assumption that deviations from ideal behavior may be attributed to the formation of aggregated species of urea.

This note provides direct experimental information on the stability in water of a model interamide hydrogen bond. Of the several approaches tried, the successful one was an examination of the infrared spectra[3] of concentrated aqueous solutions of N-methylacetamide in the region of 1.4–1.7 μ (Fig. 1). In this range glass vessels can be used, and optical densities are not too intense, so concentrated solutions can be examined in cells with precisely matched thicknesses. The absorptions of N–H and O–H groups still overlap, however, and hence the absorption of water must be compensated for. This was accomplished by the use of reference cuvettes which contained aqueous dimethylacetamide solutions at concentrations carefully selected to place the same amount of water in the light path as was present in the sample cuvette containing aqueous monomethylacetamide. Liquid dimethylacetamide is essentially transparent in the range 1.45–1.60 μ and shows peaks very comparable to those of monomethylacetamide on both flanks of this range.

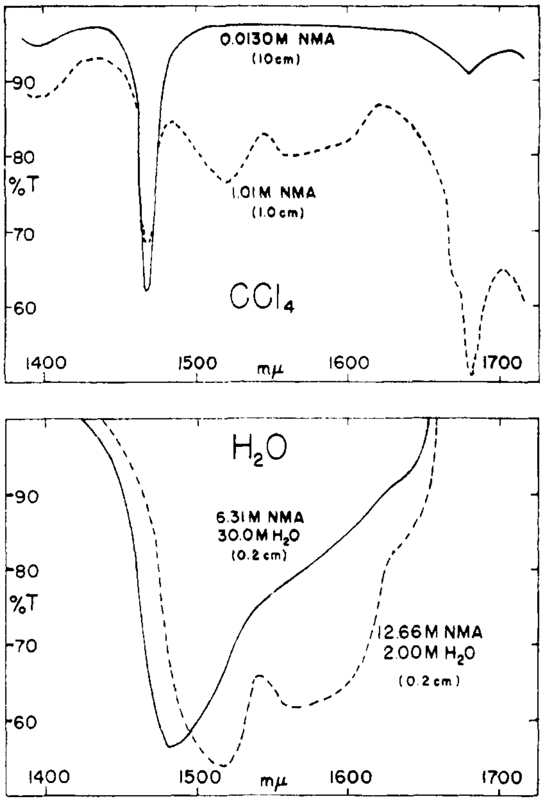
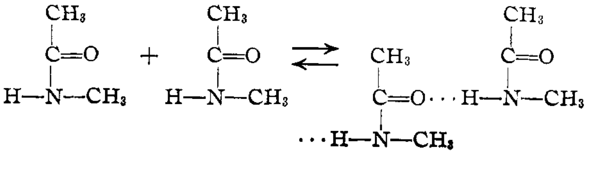


Fig. 1.—Near infrared absorption spectra of N-methylacetamide in carbon tetrachloride and in water. Water solutions contain dimethylacetamide in reference cell to balance all absorption except that of N-H of methylacetamide. Cell thickness is marked for each solution.

In Fig. 1 are illustrated spectra in relatively dilute and concentrated solutions, respectively, in each of two solvents. In carbon tetrachloride, N-methylacetamide exists as a monomer in dilute solution (∼0.01 *M*) and as such shows a sharp peak at 1.47 μ (6800 cm.$^{-1}$). In more concentrated solutions aggregation sets in



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[1] G. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, 1960.

[2] J. A. Schellman, *Compt. rend. trav. lab. Carlsberg, Ser. Chim.*, **29**, 223 (1955).

[3] Compare J. Hermans, Jr., and H. A. Scheraga, THIS JOURNAL, **82**, 5156 (1960), for another application of near infrared spectra to problems of protein structure.