

1306 (m), 1295 (m), 1197 (m), 1110 (vs), 1080 (s), 1010 (s), 915 (s), 878 (m), 860 (m), and 770 cm^{-1} (m).

Anal. Calcd for $\text{C}_6\text{H}_5\text{F}$: C, 71.97; H, 9.06. Found: C, 72.01; H, 9.25.

The formation of only one isomer (VIIId) from VIIb was confirmed by isolation and reduction (80° , AIBN) of pure VIIb, followed by glpc (Apiezon L, 65°).

7-Fluoro-2-oxanorcarane (VIIIc and VIIIId) was obtained in 33% (80° , AIBN), 60% (120 – 130° , DTBP), or 60% yield (170 – 175° , DTBP): bp 45 – 52° (30 mm); n_D^{20} 1.4352 (VIIIc) or 1.4433 (VIIIId); ir 2934 (vs), 2880 (s), 1454 (m), 1439 (m), 1403 (m), 1280 (m), 1238 (vs), 1208 (s), 1148 (s), 1085 (vs), 1035 (s), 912 (s), 880 (s), 820 (s), and 735 cm^{-1} (s).

Anal. Calcd for $\text{C}_6\text{H}_5\text{OF}$: C, 62.05; H, 7.81. Found: C, 62.19; H, 7.98.

The isomer distributions in the products were determined by glpc (Apiezon L, 80°) and are shown in Table IV.

6-Fluoro-3-oxabicyclo[3.1.0]hexane (IXc and IXd) was obtained in 36% yield (90° , AIBN): bp 51.5 – 52.5° (20 mm); n_D^{20} 1.4168 (IXc) or 1.4329 (IXd); ir 3055 (m), 2950 (s), 2895 (vs), 1483 (m), 1420 (s), 1358 (s), 1200 (m), 1182 (vs), 1110 (vs), 1078 (vs), 1020 (s), 1000 (s), 983 (vs), 900 (s), 840 (s), 815 (s), 779 (s), 719 (s), and 705 cm^{-1} (m).

Anal. Calcd for $\text{C}_5\text{H}_6\text{OF}$: C, 58.82; H, 6.91. Found: C, 58.80; H, 6.82.

The reduction of pure IXb at 90° (AIBN) or at 130 – 135° (DTBP) gave a mixture of IXc and IXd, the ratio of which (see Table III) was determined by glpc (Apiezon L, 60°).

The Reduction of 7-*exo*-Chloro-7-*endo*-fluoro-2-oxanorcarane (VIIIb) under Various Conditions. A. **Change in Reaction Temperature.**—A mixture of 6 g (0.04 mol) of VIIIb, 12.8 g (0.05 mol) of tri-*n*-butyltin hydride, and a small amount of AIBN was heated at 80° for 10 hr. The reaction mixture was submitted to glpc before distillation and the ratio of VIIIc/VIIIId was determined. The reductions at 130 and at 165° in the presence of

DTBP were carried out similarly. The results are shown in Table III.

B. **Change in Tri-*n*-butyltin Hydride Concentration.**—A mixture of 6 g (0.04 mol) of VIIIb, 10.3 g (0.04 mol) of tri-*n*-butyltin hydride, and a small amount of AIBN (or DTBP) was heated at 90° (or at 135 – 140°) for 5 hr. The isomer ratio (VIIIc/VIIIId) in the product was determined by glpc before distillation. The reductions using a three- or sixfold amount of tri-*n*-butyltin hydride were carried out similarly. The results are shown in Table V.

The Reduction of 7-*exo*-Bromo-7-*endo*-fluoro-2-oxanorcarane (Xb).—A mixture of 9.8 g (0.05 mol) of Xb and 15.4 g (0.06 mol) of tri-*n*-butyltin hydride was stirred at 20° for 10 hr, in the absence of catalyst. Distillation of the reaction mixture gave 4.6 g (80%) of 7-*endo*-fluoro-2-oxanorcarane (VIIIId), with no sign of the *exo*-fluoro isomer (VIIIc) being formed (glpc). The reduction at 80 – 90° in the absence of catalyst gave a 95% yield of a mixture of VIIIc and VIIIId, in the ratio 28:72 (glpc).

Registry No.—Tributyltin hydride, 688-73-3; Ic, 17370-50-2; IIc, 22140-48-3; IId, 22140-49-4; IIIc, 22140-50-7; IIId, 22140-51-8; IVc, 22140-52-9; IVd, 22140-53-0; Vc, 22140-54-1; Vd, 22140-55-2; VIc, 16646-98-3; VIId, 16646-97-2; VIIc, 19144-92-4; VIIId, 19144-93-5; VIIIc, 22140-60-9; VIIIId, 22140-61-0; IXc, 22140-62-1; IXd, 22140-63-2.

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A Nuclear Magnetic Resonance Analysis of Several Photodimers Containing Cyclobutane Rings

LIVIO PAOLILLO, HERMAN ZIFFER, AND OLE BUCHARDT

National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014, and Chemical Laboratory II, University of Copenhagen, The H. C. Orsted Institute, Copenhagen, Denmark

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The nmr spectra of the cyclobutane protons of the head-to-head *syn* dimer of coumarin and the head-to-head *anti* dimer of N-methylcarbostyryl have been analyzed. The analysis has demonstrated that it is possible to correlate the structure and stereochemistry of these photodimers with the coupling constants. A similar analysis of the photodimers of 6-chloro- and 6-methylcarbostyryl has been performed and their structure and stereochemistry have been assigned.

Although dimerization was one of the first observed photochemical reactions, the difficulties involved in determining the exact structures of these dimers have handicapped progress in understanding the mode and mechanism of their formation. To develop procedures that would aid and simplify the structure elucidation of photodimers containing cyclobutane rings, the nmr spectra of several such dimers have been examined. Fleming and Williams¹ have summarized the known coupling constants between protons on cyclobutane rings and their summary indicates that *cis* couplings are generally larger than *trans* couplings. However, the coupling constants vary over a sufficient range so that some overlap between the values occurs. Therefore knowledge of a single coupling constant between protons in a cyclobutane ring is frequently insufficient to establish the stereochemistry of the protons in question. We have examined the nmr spectra of several dimers of

coumarin² as well as those of dimers of carbostyryls.³ The structures of the coumarin dimers I–III and the carbostyryl dimers IVa and IVb previously have been rigorously established and it was found that each of the dimers contains four cyclobutane protons which are held in a rigid configuration by their fused six-four ring junctions.

Previous attempts to analyze the nmr spectra of the cyclobutane coumarin dimers² I, II, and III have been unsuccessful owing to their very poor solubility and because in the solvents commonly employed for nmr spectroscopy the four cyclobutane protons were found to be essentially magnetically equivalent. We have found that liquid sulfur dioxide is a good solvent for these compounds and that the previously magnetically

(2) G. O. Schenck, I. von Wilueki, and C. H. Krauch, *Chem. Ber.*, **95**, 1409 (1962); C. H. Krauch, S. Farid, and G. O. Schenck, *ibid.*, **99**, 625 (1966).

(3) (a) O. Buchardt, *Acta Chem. Scand.*, **18**, 1389 (1964); (b) O. Buchardt, P. L. Kurnler, and C. Lohse, *ibid.*, in press.

(1) I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

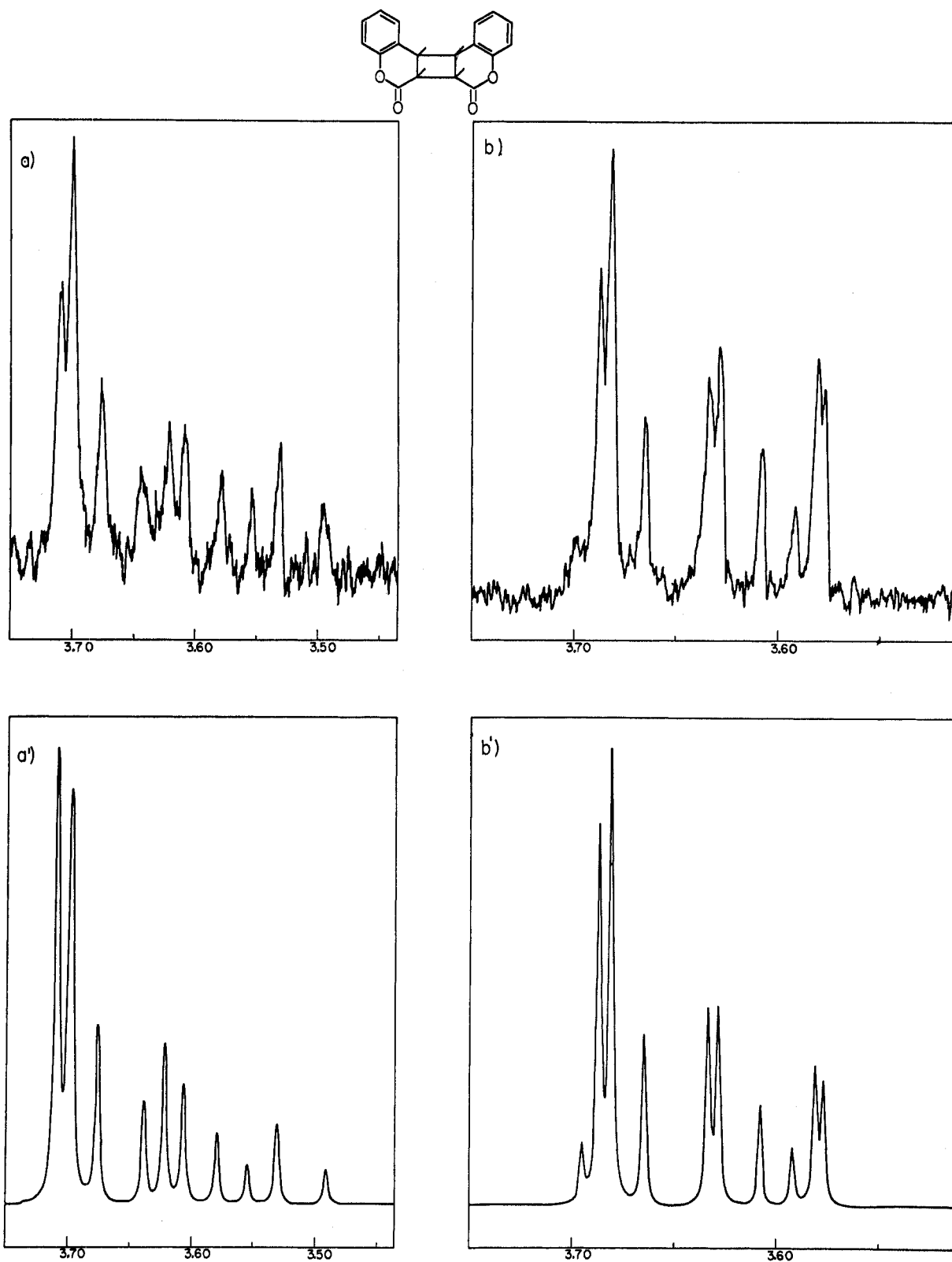


Figure 1.—The nmr spectra of the cyclobutane protons of I: (a) 60 MHz, experimental; (a') 60 MHz, calculated; (b) 100 MHz, experimental; (b') 100 MHz, calculated.

equivalent cyclobutane protons in I became magnetically nonequivalent in this solvent. The 60-MHz and 100-MHz spectra (Figure 1) show a sufficient number of transitions to permit an unequivocal assignment of the various coupling constants in an AA'BB' system. The analysis of the nmr spectra was performed using an

iterative Swalen and Reilly⁴ computer program modified for the IBM 360. A CALCOMP program was used to plot the calculated spectra to facilitate a comparison with the experimental spectra.

(4) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

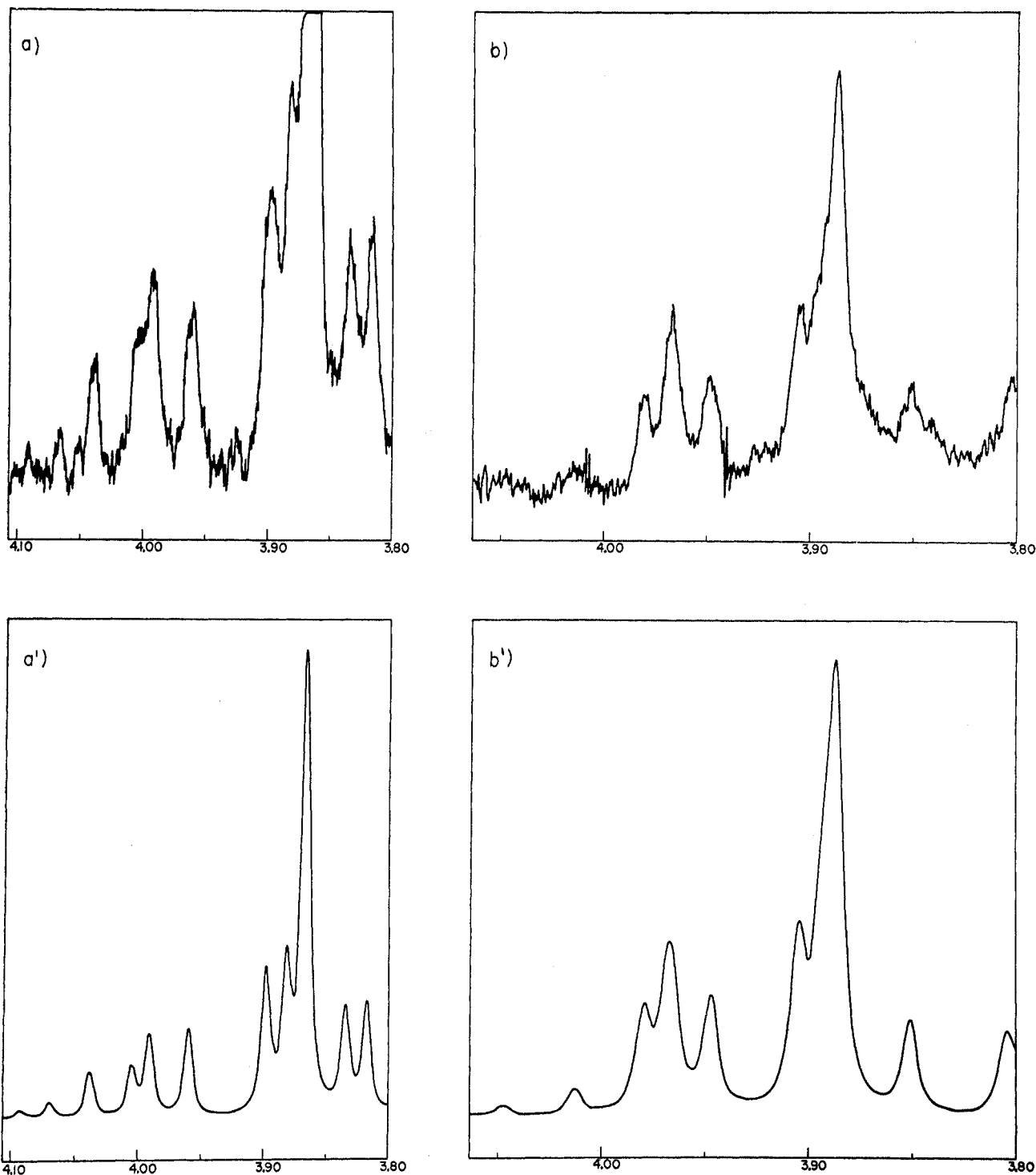
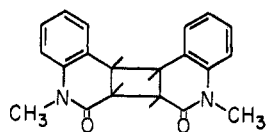


Figure 2.—The nmr spectra of the cyclobutane protons of IVb: (a) 60 MHz, experimental; (a') 60 MHz, calculated; (b) 100 MHz experimental; (b') 100 MHz, calculated.

The 100-MHz and 60-MHz spectra of compounds I and IVb were analyzed. The calculated coupling constants were considered to be correct when the values obtained for the 100-MHz spectra also gave close agreement between calculated and experimental 60-MHz spectra. This provides an additional check of

the accuracy of the calculated parameters. The observed and calculated spectra (60 and 100 MHz) of I are shown in Figure 1 and the coupling constants are listed in Table I. The analysis of the signals from the cyclobutane protons in the spectra of the other coumarin photodimers II and III was not possible because the

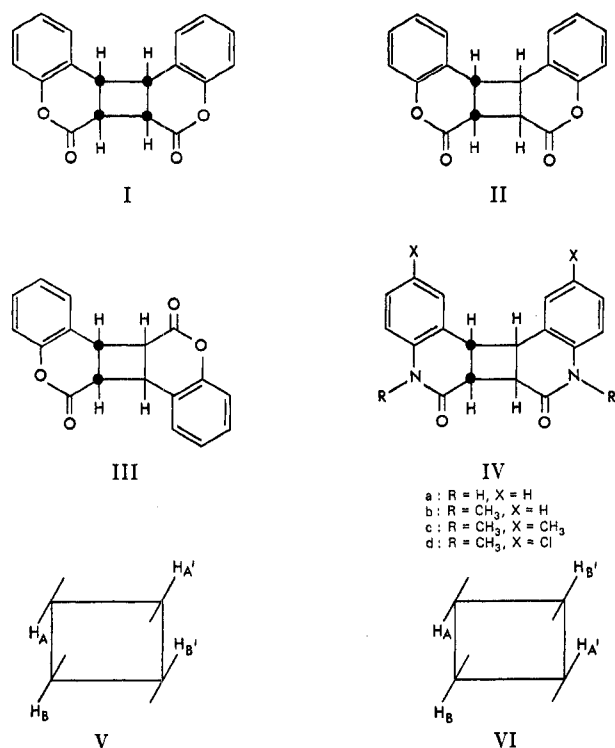


TABLE I
COUPLING CONSTANTS IN HERTZ

Compound	$J_{AA'}$	J_{AB}	$J_{AB'}$	$J_{BB'}$	A. D. ^a
I	8.28	8.56	1.47	9.97	0.06
IVb	2.97	8.77	-1.35	7.87	0.05
IVc	2.76	8.99	-0.94	7.43	0.21
IVd	2.65	8.77	-0.94	7.53	0.18

^a A. D. is the average deviation between the observed and calculated frequencies after 30 iterations.

cyclobutane protons remained essentially magnetically equivalent.

Buchardt³ has shown that carbostyryl (IVa) and N-methylcarbostyryl (IVb) on irradiation dimerize to form the h-h *anti* dimers. The original structure elucidation was sufficiently difficult as to discourage the structure determination of several substituted carbostyryl photodimers. The nmr spectrum of IVa in trifluoroacetic acid showed a sharp singlet for the four cyclobutane protons and no other suitable solvent could be found. The solubility of IVa in liquid sulfur dioxide was also poor and the cyclobutane protons were essentially magnetically equivalent. However, the photodimer of N-methylcarbostyryl (IVb) was much more soluble in sulfur dioxide and the cyclobutane protons were magnetically nonequivalent thus facilitating the analysis of the nmr spectrum. The N-methylcarbostyryl photodimer IVb was prepared using the procedure of Lederer, *et al.*,⁵ and a comparison of the observed and calculated nmr spectra is shown in Figure 2. The values of the coupling constants are summarized in Table I. It appears from Table I that there are considerable differences between the spectra of the two photodimers, I and IVb. In I, where the cyclobutane protons are in *cis, syn, cis* position, the coupling constants $^3J_{AA'}$, $^3J_{AB}$, and $^3J_{BB'}$ have comparable values in the range between 8 and 10 Hz. In IVb,

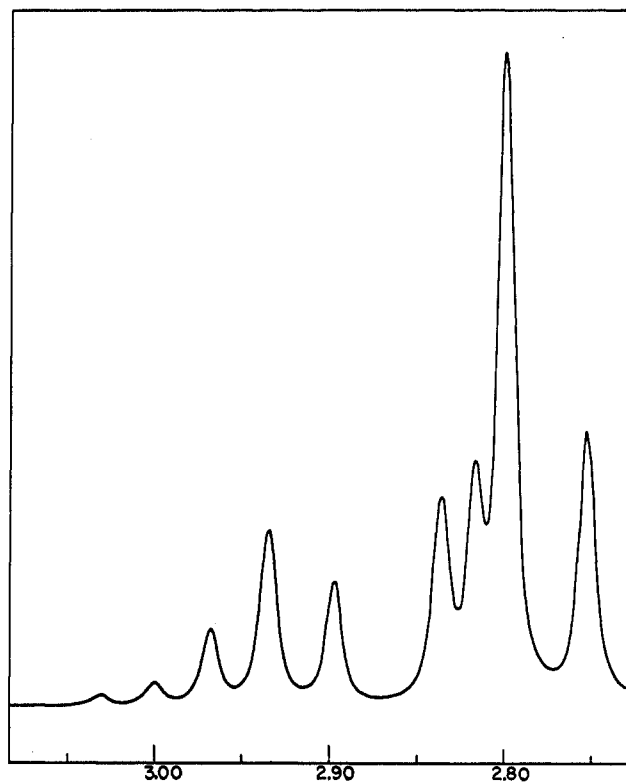
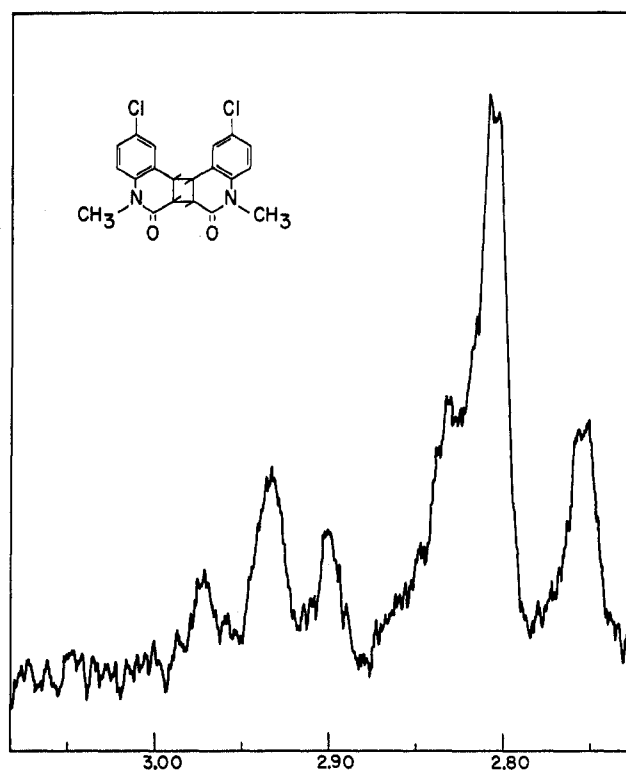


Figure 3.—The nmr spectra (60 MHz) of the cyclobutane protons of IVd: top, experimental; bottom, calculated.

where a *cis, anti, cis* configuration of the cyclobutane ring occurs, $^3J_{AA'}$ is a *trans* coupling constant which is much lower in value than the $^3J_{AA'}$ *cis* coupling constant found in I. Furthermore, the long-range coupling constant $^4J_{AB'}$ is negative in the case of the *anti* configuration, whereas it is positive in the case of the *syn* configuration of I. The $^3J_{AB}$ coupling constant corresponds to a *cis* configuration in both photodimers and

(5) B. C. Das, S. D. Gero, and E. Lederer, *Biochem. Biophys. Res. Commun.*, **29**, 211 (1967).

does not present large variations. The *trans* coupling constant ${}^3J_{BB'}$ of IVc is approximately 2 Hz less than the *cis* coupling constant ${}^3J_{BB'}$ in I. On the basis of these considerations the nmr spectral analysis of the N-methyl derivatives of substituted carbostyryl photodimers IVb and IVd (Figure 3) was performed and their nmr spectra at 60 MHz and 100 MHz were calculated. The results are shown in Table I. The coupling constants show that the dimers have formed by h-h fusion (V) rather than by h-t fusion (VI), since in the latter case $J_{AB'}$ would be considerably greater than $J_{AA'}$, whereas the reverse was found. The values of the $J_{AA'}$ coupling constants in IVc and IVd and the negative sign of the ${}^4J_{AB'}$ coupling together with the close similarity of the coupling constants to those of IVb show that the geometry of the cyclobutane ring of all three compounds is the same.

As very little information on the effect of substituents on the course of dimerization reactions is available, it is interesting to note that in these few examples the course of dimerization does not appear to be affected by the substituents. It is also important to emphasize that the choice of a suitable solvent and the analysis of the nmr spectra of these photodimers can give very useful

information about their stereochemistry which is otherwise very difficult to obtain.

Experimental Section

The nmr spectra were determined in liquid SO₂ on Varian A-60 and Varian HA-100 spectrometers, using tetramethylsilane as an internal standard.

Dimers of Coumarin.—These were prepared according to the previously published procedure.³

Dimers of Carbostyryl.—These were prepared according to the recently described procedure.³

N-Methyl Derivatives.—The N-methyl derivatives of the photodimers were prepared using the procedure of Lederer, *et al.*⁵ The N-methyl-6-chlorocarbostyryl photodimer had mp 240° from methanol.

Anal. Calcd for C₂₀H₁₆N₂O₂Cl₂: C, 62.03; H, 4.16. Found: C, 61.94; H, 4.2.

The N-methyl-6-methylcarbostyryl photodimer had mp 252–253° from ethyl acetate.

Registry No.—I, 21044-76-8; IVb, 22040-14-8; IVc, 22040-15-9; IVd, 22040-16-0.

Acknowledgment.—We wish to thank Doctors G. O. Schenck and S. Farid for samples of the coumarin photodimers.

Small-Ring Compounds. XXII. Solvolysis of 2-Arylcyclopropylcarbinyll 3,5-Dinitrobenzoates

TATSUYA SHONO, IKUZO NISHIGUCHI, AND RYOHEI ODA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

Received March 6, 1969

A series of *trans*-2-arylcyclopropylcarbinyll 3,5-dinitrobenzoates was synthesized and solvolyzed in 75 wt % aqueous dioxane at 130°. The Hammett plot of the relative rates gave a straight line with slope -1.5 , suggesting a substantial extent of delocalization of the positive charge to the 2 position of the cyclopropylcarbinyll cation. A bisected-type cation was suggested for the conformation of 2-arylcyclopropylcarbinyll cation.

The character of cyclopropylcarbinyll cation has been studied extensively by several workers.¹ Bicyclobutonium ion, bisected cation, or homoallylic cation have been proposed as a conformation of the cyclopropylcarbinyll cation in order to explain the somewhat peculiar property of the cation. On the other hand, it has been reported in some of the early literature that the cyclopropylcarbinyll cations bearing substituents showed substantially different behavior from that of the nonsubstituted cation. For example, the main product obtained in the deamination of cyclopropylcarbinyllamine- α -¹⁴C was an equimolar mixture of cyclobutanol and cyclopropylcarbinol, in which the carbon isotope was substantially scrambled,² while the deamination of 1-methylcyclopropylcarbinyllamine- α -¹⁴C gave 1-methylcyclobutanol as the exclusive product, showing a minor extent of the isotope scrambling.³

In another investigation, the attachment of a phenyl or methyl group to the 1 position of the cyclopropylcarbinyll cation caused a considerable change in the activation entropy of the formation of the cation.⁴

An electron-donating group substituted in the α position of the cyclopropylcarbinyll cation remarkably stabilizes the cation and prevents the skeletal rearrangement of the ring under the solvolytic conditions.⁵ On the other hand, the same group attached to the 1 position of the cation makes only a minor contribution to the stabilization of the cation and brings on the formation of the corresponding cyclobutyl product.⁶ Thus, it is conceivable that the character of the substituted cyclopropylcarbinyll cation is substantially influenced by the property and location of the substituent. Thus far, little attention has been focused on the role of the substituent in the 2 position of the cation. The effect of a methyl group substituted in the 2 position has been studied by Schleyer and coworker, and a bisected-type conformation has been suggested for the cation.¹ Sneen has reported that a phenyl substituent in the 2 position of cyclopropylcarbinyll cation showed no remarkable influence on the stability of the cation.⁷

In the present study, the role of a phenyl group attached to the 2 position of the cyclopropylcarbinyll cation and the conformation of some 2,2- or 2,3-disubstituted cations were studied.

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