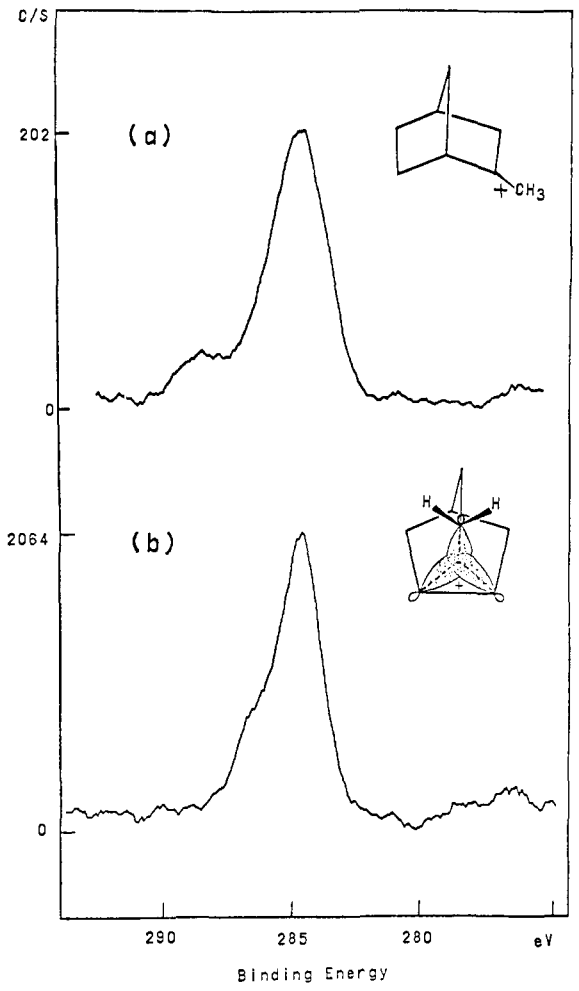
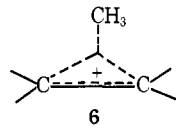


Figure 1. Carbon 1s electron spectrum of norbornyl cation **1** (lower trace) and 2-methylnorbornyl cation **4** (upper trace).

smaller separation of 3.7 eV (with an intensity ratio of ~1:7) which indicates that in spite of the stabilizing effect of the methyl group, there is some σ delocalization in the bicyclo[2.2.1]heptyl system.

An essentially different carbon 1s electron spectrum is obtained for the parent norbornyl cation **1** (Figure 1, lower trace). There is a single broad line with a pronounced shoulder on the higher binding energy side (corresponding to C_2 and C_6). A curve resolver analysis gave an approximate intensity ratio of 2:5 and a maximum separation of 1.7 eV. These results clearly suggest that the ion **1** is of "nonclassical" carbonium ion nature since no high-binding energy line characteristic of a carbenium center is found. An equilibrating classical structure **1a** $\rightleftarrows$ **1b** should give an electron spectrum identical with a static "classical" carbenium ion, even under conditions of extremely rapid equilibration. For example, the rapidly equilibrating, degenerate cyclopentyl cation clearly shows the carbenium center line separated from the methylene carbons. The results obtained for the norbornyl cation are in excellent agreement with reported carbon-13 and proton magnetic resonance, as well as Raman spectroscopy data on the long-lived norbornyl cation, which all strongly support the methylene-bridged pentacoordinated carbonium ion or "nonclassical" nature of the norbornyl cation.[4]

(4) (a) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3958 (1969), and references cited therein. (b) Moreover, *ab initio* calculations[5] on model $C_8H_7^+$ ions show that in structure **6** the difference in carbon 1s



6

electron binding energy between the bridged methyl and adjacent methylene groups is *ca.* 1.1 eV. This value is consistent with our experimental results.

Table I. Binding Energy Differences of Carbocation Centers from Neighboring Carbon Atoms (dE_{b^+C-C})

Ion	dE_{b^+C-C}	Approximate rel C^+/C intensity
$(CH_3)_3C^+$	3.9 ± 0.2	1/3
5		
3	4.2 ± 0.2	1/5
4	3.7 ± 0.2	1/7
2	4.3 ± 0.5	1/4
1	1.7 ± 0.2	2/5

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For a correlation between nmr and electron spectroscopy, see G. D. Mateescu, Abstracts, Papers of the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1972, No. 237; G. D. Mateescu and J. L. Riemenschneider, Abstracts of Papers, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, No. ORGN-115.

(5) We thank Professor J. Pople, Dr. L. Radom, and Professor P. v. R. Schleyer for communicating their results prior to publication.

(6) NIH postdoctoral fellow.

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Anomerization of Glycosyl Azides in a Two-Step 1,3-Dipolar Cycloaddition Reaction

Sir:

We wish to report the first instance in which a substituted azide has been demonstrated to undergo a two-step 1,3-dipolar cycloaddition. The synthesis of *vic*-triazoles by an azide cycloaddition to cyanoacetamide has been known for many years.[1-3] The mechanism of these 1,3-dipolar cycloaddition reactions has, however, remained obscure. Recent investigations in our laboratory of an unusual rearrangement of glycosyl azides have provided evidence to clarify the cycloaddition mechanism of substituted azides with 2-substituted acetonitrile derivatives.

The preparation[4] of 2,3,5-tri-*O*-benzyl-β-D-arabino-

(1) O. Dimroth, *Ber.*, **35**, 1029 (1902).

(2) J. R. E. Hoover and A. R. Day, *J. Amer. Chem. Soc.*, **78**, 5832 (1956).

(3) A. Dornow and J. Helberg, *Chem. Ber.*, **93**, 2001 (1960).

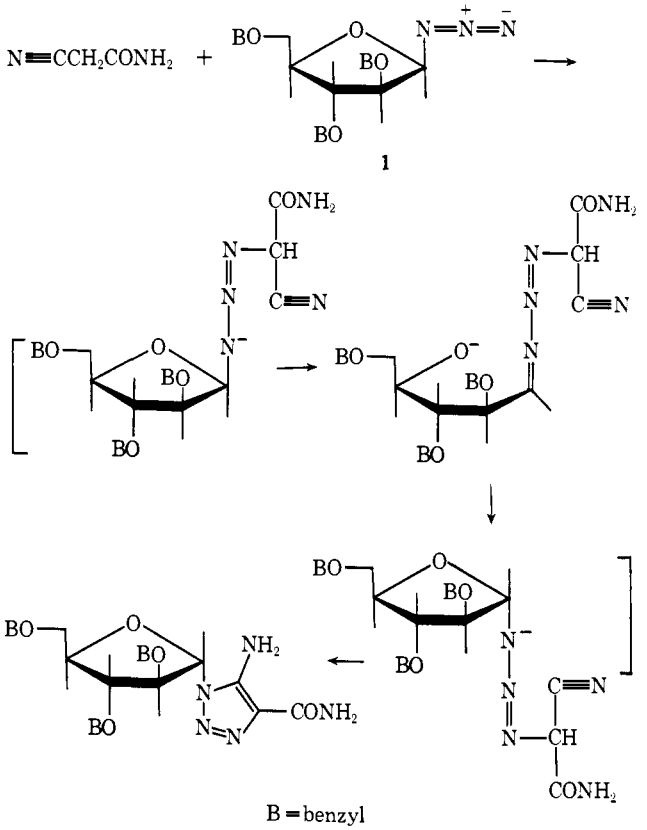
(4) All new compounds reported gave elemental analyses consistent with assigned structures; the complete physical, spectral, and optical properties will be reported in the full paper.

Table I. Ultraviolet Spectral Data (λ_{max}, nm) of Some *vic*-Triazole and *vic*-Triazolo[4,5-*d*]pyrimidine Nucleosides

	Acid	Base		Acid	Neutral
5-Amino-1-(2,3,5-tri-*O*-benzyl-α-D-arabinofuranosyl)-4-carbamoyl-*vic*-triazole (**3**)	262	235, 259	5-Amino-4-carbamoyl-1-methyl-*vic*-triazole		227, 260
5-Amino-1-(2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-4-carbamoyl-*vic*-triazole (**4**)	261	236, 259	5-Amino-4-carbamoyl-3-methyl-*vic*-triazole	273	
7-Amino-3-α-D-arabinofuranosyl-*vic*-triazolo[4,5-*d*]pyrimidine (**5**)	261	278	7-Amino-1-methyl-*vic*-triazolo-[4,5-*d*]pyrimidine	284	285
7-Amino-3-β-D-arabinofuranosyl-*vic*-triazolo[4,5-*d*]pyrimidine (**6**)	262	278	7-Amino-3-methyl-*vic*-triazolo-[4,5-*d*]pyrimidine	264	277

furanosyl azide (**1**) and the corresponding α-anomer **2** was accomplished[5] by treatment of 2,3,5-tri-*O*-benzyl-D-arabinofuranosyl chloride with sodium azide in acetonitrile. Assignment of the anomeric configuration of **1** and **2** was made on the basis of optical rotations and nmr studies.

When the α-azide (**2**) was treated with KOH and cyanoacetamide in aqueous DMF at room temperature, there was only one isolable product (**3**, 85% yield). The β-azide (**1**) underwent a similar reaction to give *two* products, **3** and **4** (72 and 5% yields, respectively), which were separated by column chromatography in the ratio of 14:1. The major product **3** was identical in all respects with the product of the α-azide cycloaddition reaction.



Comparison of the uv maximum of **3** and **4** (259 nm) with the maximum of 5-amino-4-carbamoyl-1-methyl-*vic*-triazole (260 nm)[6] and 5-amino-4-carbamoyl-3-methyl-*vic*-triazole (273 nm)[7] permitted identification of both **3** and **4** as N^1-alkylated triazole derivatives. This structural assignment was confirmed by ring closure of **3** and **4** to their adenosine analogs, **5** and **6**, by a multistep procedure.[5]

The uv spectral maximum (see Table I) of the adenosine analogs [**5** and **6** (278 nm)] was dissimilar with the maximum of 7-amino-1-methyl-*vic*-triazolo[4,5-*d*]-pyrimidine (285 nm),[7] but was in good agreement with the values reported for 7-amino-3-methyl-*vic*-triazolo-[4,5-*d*]pyrimidine (277 nm),[8] thereby indicating glycosylation on N^3 (N^1 of *vic*-triazole).

Since isomerization to the pyranose sugar could not have occurred in the presence of the benzyl blocking groups, the two products of the β-azide cycloaddition reaction were assigned the structures of 5-amino-1-(2,3,5-tri-*O*-benzyl-α-D-arabinofuranosyl)-4-carbamoyl-*vic*-triazole (**3**, major) and the corresponding β anomer (**4**, minor).

Debenzylation of **3** and **4** with sodium in liquid ammonia gave the free triazole nucleosides, **7** and **8**. Oxidation of **7** and **8** with sodium periodate followed by reduction with sodium borohydride gave compounds whose optical rotations were equal in magnitude (within experimental error) but opposite in sign, confirming that **3** and **4** differed only in the configurations about C-1′.

Ring closure of **3** with diethoxymethyl acetate and subsequent debenzylation gave 3-α-D-arabinofuranosyl-*vic*-triazolo[4,5-*d*]pyrimid-7-one (**9**). Periodate oxidation of **9** followed by reduction with borohydride gave a derivative whose optical rotation was equal in magnitude (within experimental error), but opposite in sign to the optical rotation of the reduced product of the periodate oxidation of 8-azainosine (3-β-D-ribofuranosyl-*vic*-triazolo[4,5-*d*]pyrimid-7-one, known to possess the β configuration),[9] thereby confirming the α assignment to **3**. A similar reaction sequence was performed on **4** and the optical rotation obtained was equal in magnitude (within experimental error) and sign as that obtained from 8-azainosine.

Glycosyl azides have been presumed[10,11] to react without inversion of the anomeric center, *i.e.* by a concerted mechanism. The isolation of anomerically pure azide starting material from a reaction terminated before completion indicated that anomerization of starting material did not occur under reaction conditions. Similarly, when either of the product triazole

(5) C. W. Smith, R. K. Robins, and R. L. Tolman, *J. Med. Chem.*, in press.
(6) A. Albert, *J. Chem. Soc. C*, 2076 (1968).
(7) A. Albert and K. Tratt, *ibid.*, 344 (1968).
(8) A. Albert, *ibid.*, 152 (1969).
(9) W. Hutzenlaub, R. L. Tolman, and R. K. Robins, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. MEDI-41.
(10) G. Garcia-Munoz, J. Iglesias, M. Lora-Tamayo, and R. Madronero, *J. Heterocycl. Chem.*, **5**, 699 (1968).
(11) R. E. Harmon, R. A. Earl, and S. K. Gupta, *J. Org. Chem.*, **36**, 2553 (1971).

nucleosides (**3** or **4**) was exposed to the reaction conditions for extended periods of time, no anomerization could be detected. Therefore, rearrangement of a reaction intermediate must have occurred. In contrast to the widely observed concerted azide 1,3-dipolar cycloadditions,[12,13] the conversion of the β-glycosyl azide (**1**) to an α-triazole nucleoside **3** must be a multistep process. We suggest a two-step mechanism in which the first step is attack by the carbanion generated from cyanoacetamide on the electrophilic terminal nitrogen[13] of the glycosyl azide, followed by attack of the azide nitrogen adjacent to the sugar on the carbon of the nitrile group. Rearrangement of the intermediate, formed after attack of the cyanoacetamide carbanion, could occur by delocalization of the negative charge from the C-adjacent nitrogen to the furanose-ring oxygen. Thus, the C–N bond of the glycosyl azide would possess some double bond character, thereby permitting anomerization of C-1 and relief of the 1,2 interaction in the furanose ring before the second step occurs.

(12) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).
(13) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963); *Chem. Ber.*, **98**, 1138 (1965); **99**, 475 (1966).

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Preparation of Cycloocta[*def*]biphenylene, a Novel Benzenoid Antiaromatic Hydrocarbon[1]

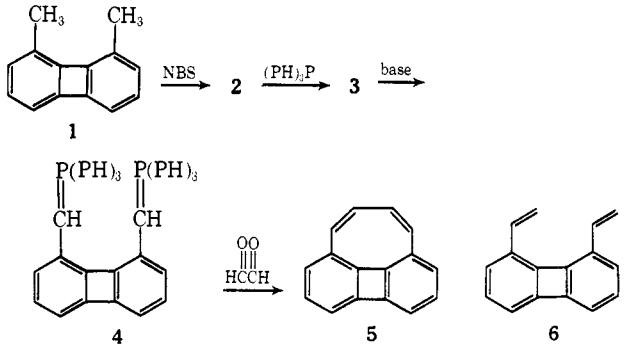
Sir:

There has been considerable interest in the properties of fused $(4n + 4n)\pi$ networks. Although their predicted stability is intermediate between aromatic and antiaromatic networks,[2] the few known examples appear to have physical properties characteristic of polyolefins.[3] We wish to report the preparation of the first example of a hydrocarbon containing an $(8 + 4)\pi$ network that shows definite antiaromatic properties.

1,8-Dimethylbiphenylene (**1**) was converted with NBS to the dibromide **2** in 60–80% yield: mp 150–175° dec; nmr ($CDCl_3$) τ 3.2–3.5 (3 H, m), 5.51 (2 H, s). The dibromide was difficult to purify and decomposed on a silica gel column. It was converted into the bisphosphonium salt **3** with triphenylphosphine. Treatment of **3** with *n*-butyllithium in THF, or better with dimsylsodium in DMSO, gave a solution of the bisylide **4**. When a freshly prepared ether solution of glyoxal monomer was added slowly to the solution a complex mixture of products was formed. From this mixture the title compound **5** could be isolated by column chromatography in 1% yield (12% with dimsylsodium): mp 99–100°.

(1) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 12, 1971.
(2) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, 74, 4579 (1952); A. Rosowsky, H. Fleischer, S. T. Young, R. Partch, W. H. Saunders, Jr., and V. Boekelheide, *Tetrahedron*, **11**, 121 (1960); R. Breslow, *Chem. Eng. News*, 43 (26), 90 (1965); C. F. Wilcox, Jr., *Tetrahedron Lett.*, 795 (1968).
(3) R. Breslow, W. Horspool, H. Sugiyama, and W. Vitale, *J. Amer. Chem. Soc.*, **88**, 3677 (1966); J. A. Elix, M. V. Sargent, and F. Sondheimer, *ibid.*, **89**, 5080 (1967); G. Schroder and H. Rottele, *Angew. Chem., Int. Ed. Engl.*, 7, 635 (1968); P. J. Garratt and R. H. Mitchell, *Chem. Commun.*, 719 (1968).

1,8-Divinylbiphenylene was prepared by an analogous route, in quantitative yield, from the bisylide **4** and formaldehyde: mp 104–106°; nmr (CCl_4) τ 3.0–3.6 (2 H, m), 4.2–4.8 (1 H, m); ir max (KBr) 1380, 1240, 988, 970, 907, 780, and 720 cm^{-1}; mass spectrum *m/e* (rel intensity) 204 (100), 203 (36), 202 (58), 189 (24), 181 (19), 169 (18), 131 (32), 119 (33).



Hydrogenation of **5** gave a yellow $C_{16}H_{14}$ hydrocarbon (*m/e* 206) with nmr absorptions having chemical shifts characteristic of an alkylated biphenylene: nmr (CCl_4) τ 3.3–3.8 (6 H, ABC),[4] 7.5 (4 H, m), 8.3 (4 H, m). The spectral data for **5** were consistent in all respects with those predicted for the assigned structure: high-resolution mass spectrum *m/e* 202.0778, 101.0392, and 101.5409;[5] nmr τ 3.6–4.4 (6 H, ABC),[4] 5.38 (4 H, d); uv λ_{max} (log ϵ) (cyclohexane or methanol) 621 nm (1.63[6]), 305 (4.31), 225 (4.35).

Calculations predict that **5** should be highly reactive toward electrophiles, yet be thermally stable. Preliminary evidence indicates that **5** is sensitive to both proton acids and strong Lewis acids, reacts readily with bromine, and reacts somewhat less vigorously with acetyl chloride–stannic chloride. Because of the small samples of **5** available at this time, we have been unable to identify the products unambiguously.[7]

Ring current calculations[8] suggest that **5** should have dominating paramagnetic contributions from both the four- and eight-membered rings and slight diamagnetic contributions from the benzenoid rings. 1,8-Divinylbiphenylene (**6**) showed nmr absorption near τ 3.3[4] (6 H) and an analyzable ABC multiplet (6 H) with chemical shifts of τ 3.26, 4.38, and 4.68. Apparently the closing of the eight-membered ring in going from **6** to **5** produces a marked (0.9–2.0 ppm) upfield shift in the olefinic protons as well as for the aromatic protons. Still larger shifts are found if dibenzo[*a*,*c*]cyclooctatetraene[9] is used as a reference (τ 2.82 (8 H), 3.35 (2 H), 4.00 (2 H)). These shifts are very much larger than those observed in earlier examples of $(4n + 4n)\pi$ networks, presumably reflecting the geometrically enforced planarity of the present hydrocarbon. We believe **5** is the first known example of a $(4n + 4n)$ hydrocarbon showing unmistakable antiaromatic properties. We also believe **5**

(4) This portion of the spectrum could be analyzed fully to yield coupling constants typical of the biphenylene nucleus.
(5) The last pair of peaks are in a ratio consistent with the formation of a $C_{16}H_{10}$ dication.
(6) The band at 621 nm is the beginning of a series of sharply defined vibrational steps to 327 nm (log ϵ 2.91). The 305-nm band also shows considerable fine structure.
(7) Details of these calculations and experimental results will be presented in a full paper.
(8) R. McWeeny, *Mol. Phys.*, 1, 311 (1958).
(9) J. Wolpers, Ph.D. Thesis, 1964, University of Cologne.