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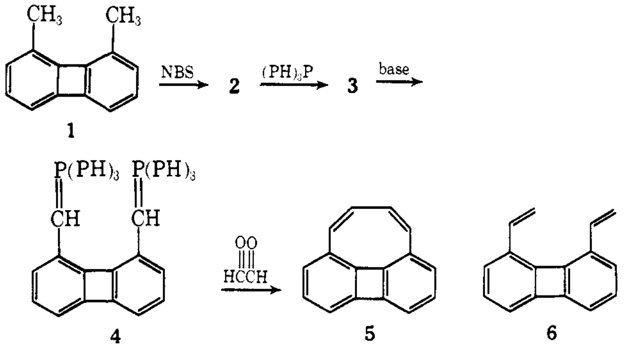
Preparation of Cycloocta[*def*]biphenylene, a Novel Benzenoid Antiaromatic Hydrocarbon[1]

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°.

1,8-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**

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[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).

[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.

will prove to be the first example of a planar cyclooctatetraene ring.[10]

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(10) X-Ray analysis of **5** is being pursued.

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Axial Pseudoasymmetry in Sulfenamides. A Method for Assignment of Configuration to *meso* and *dl* Secondary Amines[1]

Sir:

Molecules containing pseudoasymmetric carbon atoms have been objects of interest to organic stereochemists for many years.[2] Although planar and axial pseudoasymmetries were discussed some time ago,[2d] it has been only recently that examples of planar and axial pseudoasymmetry have been reported.[3,4] Planar pseudoasymmetry has been investigated in the ferrocene[3] and cyclophane[4] systems, and axially pseudoasymmetric biphenyls[4] have been reported. In the present paper we wish to report the first example of axial pseudoasymmetry in the S–N bond in a sulfenamide and to demonstrate the application of sulfenamide pseudoasymmetry in making unambiguous configurational assignments to the *meso* and *dl* diastereomers of secondary amines.

The considerable torsional barrier at the S–N bond in 2,4-dinitrobenzenesulfenamides renders the sulfenamide bond a chiral axis in sulfenamides of the general form $RSNR^1R^2$ ($R = 2,4\text{-}(NO_2)_2C_6H_3$, $R^1 \neq R^2$).[5] In such compounds torsion about the S–N bond effects racemization and rates of degenerate racemization can be measured by D nmr spectroscopy. When one of R^1 and R^2 is chiral, torsional diastereomerism is possible and is manifest in nmr[1,6,7] and ORD–CD spectra.[7] It was of interest to us to examine sulfenamides wherein R^1 and R^2 are identical or enantiomeric chiral substituents. In the latter case the sulfenamide bond is an element of axial pseudoasymmetry while in the former it is neither an asymmetric nor a pseudoasymmetric axis.

The two amines chosen for this study were the *meso* and *dl* isomers of bis-α-phenylethylamine (**1**).[8] Conversion to the 2,4-dinitrobenzenesulfenamides (**2**) was accomplished by reaction with 2,4-dinitrobenzenesulfenyl chloride.[9]

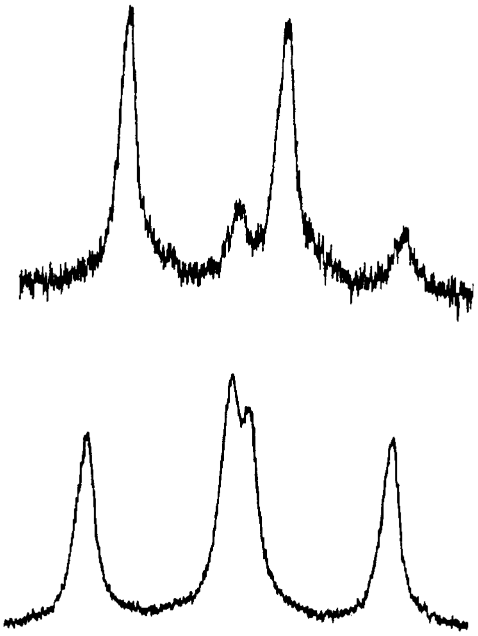

Figure 1. Portions of the nmr spectra of **2** (in $CDCl_3$ at 50°) featuring resonances due to the *C*-methyl groups: upper curve, *meso*-**2**; lower curve, *dl*-**2**.

The sulfenamide axis is a unit of pseudoasymmetry in *meso*-**2**, and torsion about the S–N bond converts one *meso* diastereomer into another. The presence of pseudoasymmetry is readily apparent in the nmr spectrum of *meso*-**2** (Figure 1). Two *C*-methyl doublets are present in a ratio of 4.5:1, the equilibrium constant for interconversion of the *R* and *S meso* isomers.[10] Each *meso* isomer gives rise to only one *C*-methyl doublet since the two methyl groups in each isomer lie on opposite sides of the σ plane and are enantiotopic. The nmr spectrum of *dl*-**2** also features two *C*-methyl doublets with identical integrated intensities.[10] There is only one diastereomer present, since rotation about the S–N bond does not generate a new isomer. However, *dl*-**2** possesses no symmetry elements and the two *C*-methyl groups are diastereotopic.

When the temperature is increased so that torsion about the S–N bond becomes rapid on the nmr time scale, coalescence is observed.[11] The free energies of

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[1] Stereochemistry in Trivalent Nitrogen Compounds. XVII. Part XVI: M. Raban, E. H. Carlson, S. K. Lauderback, J. M. Moldowan, and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, in press.

[2] (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 28; (b) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, p 91; (c) H. Hirschmann and K. R. Hanson, *J. Org. Chem.*, **36**, 3293 (1971); (d) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem.*, 78, 413 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

[3] S. J. Goldberg and W. D. Bailey, *J. Amer. Chem Soc.*, **93**, 1046 (1971).

[4] G. Helmchen, quoted in V. Prelog, *Chem. Brit.*, **4**, 382 (1968); 21st Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, 1969, Abstracts, pp 82–84.

[5] (a) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 6677 (1969). (b) M. Raban and F. B. Jones, Jr., *ibid.*, **93**, 2692 (1971).

[6] M. Raban, G. W. J. Kenney, Jr., J. M. Moldowan, and F. B. Jones, Jr., *ibid.*, **90**, 2985 (1968).

[7] M. Raban and S. K. Lauderback, *ibid.*, **93**, 2781 (1971).

[8] The two isomers were isolated from their commercially available mixture (Aldrich) by fractional crystallization of the benzoate salts from isopropyl alcohol: *meso*-**1** benzoate, mp 104–106°; *dl*-**1** benzoate, mp 135–136°. The commercial mixture was found by nmr to be composed of 65% of the *dl* isomer in which the *C*-methyl doublet resonates at higher field and 35% of the *meso* isomer. The configurational assignments were made on the basis of the nmr spectra of the 2,4-dinitrobenzenesulfenamides, *vide infra*.

[9] All new compounds had satisfactory elemental analyses and spectral data were in accord with assigned structures: *meso*-**2**, mp 187–188°; *dl*-**2**, mp 133–134°.

[10] The two *meso*-**2** doublets were centered at δ 1.53 ($J_{\text{vic}} = 6.7$ Hz) (major isomer) and 1.45 ($J_{\text{vic}} = 7.0$ Hz) (minor isomer); the two *dl*-**2** doublets were centered at δ 1.40 ($J_{\text{vic}} = 6.6$ Hz) and 1.49 ($J_{\text{vic}} = 6.6$ Hz).

[11] Although the type of conformational change, torsion about the S–N bond, and the consequences in the nmr spectra are the same for both *dl*-**2** and *meso*-**2**, the stereochemical descriptions of the events associated with coalescence are distinct. Coalescence in the spectrum of *meso*-**2** is associated with the rapid reversible interconversion of two diastereomers and the coalescing peaks correspond to methyl groups in different molecules. On the other hand, the coalescence in *dl*-**2** is a topomerization[12] and the coalescing peaks derive from methyl groups in the same molecule.