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 (71) W. P. Jencks, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **24**, S-50 (1965); E. M. Arnett, W. B. Kover, and J. V. Carter, *J. Amer. Chem. Soc.*, **91**, 4028 (1969); J. L. Neal and D. A. I. Goring, *J. Phys. Chem.*, **74**, 658 (1970); F. Franks and D. S. Reid in "Water: A Comprehensive Treatise," Vol. II, F. Franks, Ed., Plenum Press, New York, N.Y., 1973, p 323.
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Communications to the Editor

Synthesis of Dimethylbisdehydrooxa- and -thia[13]annulenes. Configurational and Conformational Isomerism in Conjugated 13-Membered Heterocycles¹

Sir:

There has been considerable interest in recent years in the synthesis of higher vinylologs of heterocycles of the pyrrole-furan-thiophene type. Such compounds may be diatropic ("aromatic") if they are $(4n + 1)$ membered and paratropic ("antiaromatic") if they are $(4n - 1)$ membered, provided the heteroatom can contribute two π -electrons to the delocalized system. Until now, the only monocyclic members to show ring current effects are the diatropic aza[9]-,² aza[13]-,^{3,4} and aza[17]annulenes,³ and their anions.^{3,5} We now describe the synthesis of the stereoisomeric dimethylbisdehydrooxa[13]annulenes **13** and **19**,⁶ and -thia[13]annulenes **14** and **20**. The di-trans sulfide **14** proved to be diatropic and is the first monocyclic nonnitrogenous member of this series to show a ring current.

Treatment of **1**⁷ in THF with 2 mole equiv of *n*-C₄H₉Li at -60° and reaction of the resulting bis ylid with 2 mole equiv of **3**⁸ at this temperature (followed by warming to 20°) led to a mixture of **5**, **10**, and the corresponding di-cis stereoisomer^{9a} (main λ_{\max} (ether) 300 nm) (Scheme I). Coupling of the mixture with Cu(OAc)₂ in pyridine at 50° for ~ 1 hr gave 1.5% (based on **1** and **3**) of the relatively stable di-trans oxa[13]annulene **13**^{9b} (pale yellow oil; *m/e* 196; λ_{\max} (ether) 272 (ϵ 18,800), 345 nm (3400)) and 1.2% of the very unstable cis,trans isomer **19**^{9b} (pale yellow oil which rapidly darkens; ¹H nmr (CDCl₃, 60 MHz), τ 3.2–4.6 m (olefinic), 8.05 s br (CH₃)).

Conversion of **2**⁷ to the corresponding bis ylid by reaction in ether with 2 mol equiv of *n*-C₄H₉Li at 20° , followed by

Scheme I

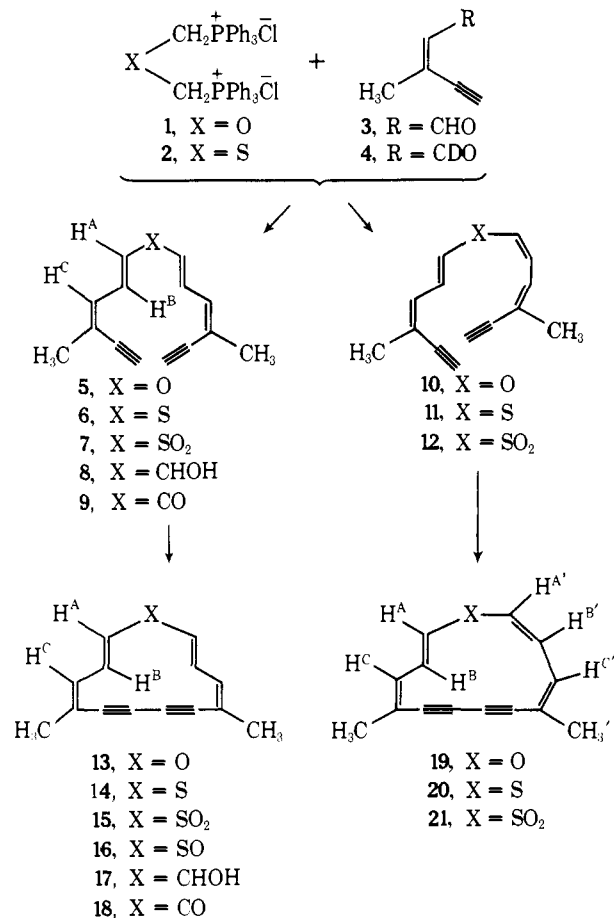


Table I. ¹H Nmr Parameters of **13**–**18** at 100 MHz in CDCl₃ (τ Values; Internal Standard, TMS; *J* Values in Hz in Parentheses)

Compd	H ^A	H ^B	H ^C	CH ₃
13 , O	3.87 d (13.5)	5.09 dd (9.5, 13.5)	3.14 d (9.5)	7.90 s
14 , S	4.49 d (15)	5.40 dd (9, 15)	2.80 d (9)	7.71 s
15 , SO ₂	5.05 d (14)	2.90 dd (5, 14)	3.07 d (5)	7.87 s
16 , SO	5.28 d (16)	3.32 dd (5, 16)	3.10 d (5)	7.90 s
17 , CHOH	5.52 d (15.5)	3.90 dd (5, 15.5)	3.32 d (5)	8.01 s
18 , CO	3.93 d (17)	0.64 dd (9.5, 17)	3.74 d (9.5)	8.29 s
Δ (13 – 5), O	+0.56	+1.35	–0.60	–0.15
Δ (14 – 6), S	+0.85	$\sim +1.8^a$	–0.93	–0.37
Δ (15 – 7), SO ₂	+1.35	+0.52	–0.56	–0.08
Δ (17 – 8), CHOH	+1.26	+0.61	–0.41	–0.06
Δ (18 – 9), CO	+0.35	–1.71	+0.17	+0.28

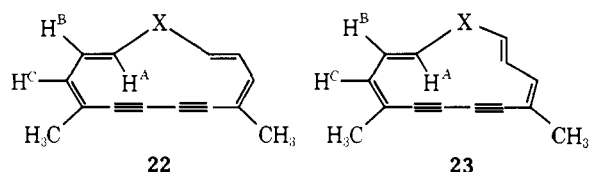
^a The H^B signal in **6** could not be located precisely.

treatment with 2 mol equiv of **3** at this temperature yielded a mixture of **6**, **11**, and the di-cis stereoisomer^{9a} (*m/e* 214; main λ_{\max} (ether) 337 nm). Coupling of this mixture essentially as before gave 2.9% (based on **2** and **3**) of the stable di-trans thia[13]annulene **14**^{9b} (yellow needles;¹⁰ *m/e* 212; λ_{\max} (ether) 295 (ϵ 37,200), \sim 305 sh (33,900), \sim 380 sh nm (3700)) and 2.2% of the unstable cis,trans isomer **20**^{9b} (yellow oil; *m/e* 212; λ_{\max} (ether) 238 (ϵ 19,100), 295 nm (9100); ¹H nmr (CDCl₃, 60 MHz), τ 2.92 d (J = 15 Hz, H^A), 3.48 d (J = 10 Hz, H^A), 2.7–4.4 m (other olefinic), 8.10 s, 8.25 s (CH₃, CH₃')).

Oxidation of **14** with excess *m*-chloroperbenzoic acid in CH₂Cl₂ at 20° for 2 hr led to 83% of the sulfone **15**^{9a} (very pale yellow needles;¹⁰ *m/e* 244; λ_{\max} (ether) 265 (ϵ 14,800), \sim 279 sh (12,000), \sim 312 sh (5600), 331 nm (5900)). Similar oxidation of **20** at 20° for 1 hr gave 82% of the sulfone **21**^{9a} (yellow needles;¹⁰ *m/e* 244; λ_{\max} (ether) 252 (ϵ 9400), 262 (9700), \sim 275 sh (8500), \sim 315 sh (2700), \sim 335 sh nm (2300); ¹H nmr (CDCl₃, 60 MHz), τ 2.80 dd (J = 10, 15 Hz, H^B), 2.97 d (J = 15 Hz, H^A), 3.45 d (J = 11 Hz, H^A), 3.53 m (H^C, H^C), 3.95 dd (J = 11, 12 Hz, H^B), 8.05 s, 8.07 s (CH₃, CH₃')). Oxidation of **14** with only \sim 1 mole equiv of *m*-chloroperbenzoic acid in CH₂Cl₂ at 0° for 1.5 hr yielded 78% of the sulfoxide **16**^{9a} (very pale yellow needles;¹⁰ *m/e* 228; λ_{\max} (ether) 263 (ϵ 16,800), 332 nm (4100)).¹¹

The ¹H nmr spectra of the di-trans heteroannulenes **13**–**16**, as well as of the related alcohol **17**^{12a} and ketone **18**,^{12b} are presented in Table I. The differences in chemical shift on passing from the acyclic models **5**–**7**^{13,14} and **8**–**9**¹² to the corresponding cyclic compounds are also given in Table I. The best ring current probe for the annulenes is provided by the "fixed" outer H^C and especially the CH₃ resonances. Compared with the shift differences of these bands in the atropic alcohol **17** (–0.41, –0.06), the sulfone **15** (–0.56, –0.08) is clearly also atropic,¹⁵ the oxide **13** (–0.60, –0.15) is at most weakly diatropic, the sulfide **14** (–0.93, –0.37) is definitely diatropic, and the ketone **18** (+0.17, +0.28) is paratropic.

That both the H^A and H^B resonances in the ¹H nmr spectrum of the diatropic sulfide **14** have shifted to higher field as compared to the acyclic model can be explained by contribution of the rotamer **22** and/or **23** with internal H^A and



external H^B, since in a diatropic molecule the shielding effect on an inner proton far exceeds the deshielding effect on an outer proton. Such rotation could indeed be demonstrated for **14** (but not for **13** or **15**) by low-temperature ¹H nmr experiments, coalescence of the H^A and H^B resonances each occurring at *ca.* –90°. Cyclization affects the H^B more than the H^A resonances in **13**, **14**, and **18**, while the reverse is true for **15** and **17**. We therefore assume that the conformations indicated for **13**, **14**, and **18** (with both H^B internal) are the main contributors to the structures of these compounds but that conformations of type **22** (with both H^A internal) are the main contributors to **15** and **17**.¹⁷ This assumption is supported by the fact that $J_{B,C} = \sim$ 9.5 Hz in **13**, **14**, and **18**, but only 5 Hz in **15**, **16**, and **17**.¹⁸ The unusually high field H^A resonances in **15**, **16**, and **17** are presumably due to the anisotropy of the acetylenes, and it appears that such anisotropy can cause either an upfield or a

downfield shift, depending on the exact dispositions of the groups.¹⁹

Comparison of the ¹H nmr spectra of the cis,trans isomers **19**–**21** with those of the corresponding acyclic models **10**–**12**^{13,14} shows these heteroannulenes to be atropic, and they are presumably less planar than the di-trans compounds.

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References and Notes

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- (8) E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 937 (1946); I. Heilbron, E. R. H. Jones, and M. Julia, *ibid.*, 1430 (1949).
- (9) Isolated by chromatography on (a) Al₂O₃ (Woelm, act III); (b) SiO₂ (Woelm, act III).
- (10) The compound decomposed on attempted melting point determination.
- (11) Initially, bis(cyclohexene)-annulated derivatives of **13**–**15** and **19**–**21** were synthesized, using 2-ethynyl-1-cyclohexene-1-carboxaldehyde instead of **3** in the initial step (P. J. Beeby, R. L. Wife, and F. Sondheimer, unpublished experiments). These polycyclic substances showed similar properties to those of the corresponding monocyclic annulenes but proved to be more stable.
- (12) (a) R. L. Wife and F. Sondheimer, unpublished experiments; (b) J. Ojima and F. Sondheimer, unpublished experiments.
- (13) The acyclic sulfones **7** and **12** were prepared from the corresponding sulfides essentially as described for the cyclic sulfones **15** and **21**.
- (14) Unequivocal ¹H nmr assignments to the various protons of **5**–**7** and **10**–**12** involved, *inter alia*, the preparation of the corresponding deuterio derivatives (D instead of H^B) by use of **4** (from **3** by reduction with LiAlD₄ and then oxidation with MnO₂) instead of **3** in the first step.
- (15) The sulfoxide **16** is also atropic, since its ¹H nmr spectrum closely resembles that of the sulfone **15**.
- (16) The coalescence temperature is considerably lower than that of related conformationally mobile diatropic bisdehydro[14]annulenes, where the individual conformers could be observed at low temperature (R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 165 (1974)).
- (17) X-Ray crystallographic analyses of **14** and **15** are now in progress, in order to determine their conformation in the solid state. Preliminary results indicate that the sulfone **15** exists as conformer **22** (C. C. Chiang and I. C. Paul, private communication).
- (18) The very low value of $J_{B,C}$ in **15**, **16**, and **17** suggests that these substances exist entirely as conformation **22**, but variable temperature ¹H nmr experiments with **15** (–110 to +150°) gave no further information.
- (19) See J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); K. G. Untch and D. C. Wysocki, *ibid.*, **89**, 6386 (1967); H. A. Staab and R. Bader, *Chem. Ber.*, **103**, 1157 (1970); P. J. Beeby and F. Sondheimer, *J. Amer. Chem. Soc.*, **94**, 2128 (1972); *Angew. Chem.*, **85**, 404 (1973); J. M. Brown and F. Sondheimer, *ibid.*, **86**, 348 (1974).

Richard L. Wife, Franz Sondheimer*

Chemistry Department, University College
London WC1H 0AJ, England

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Synthesis of Bisdehydrooxa- and -thia[15]annulenes, Conjugated 15-Membered Heterocycles¹

Sir:

The preparation of potentially diatropic ("aromatic") bisdehydrooxa- and -thia[13]annulenes, described in the preceding publication,¹ encouraged us to study the synthesis of potentially paratropic ("antiaromatic") bisdehydrohetero[15]annulenes by similar methods. We now report the synthesis of the bisdehydrothia[15]annulenes **7** and **18**, as