support of the work and to the National Science Foundation and Procter and Gamble Co. for fellowship support.

Registry No.—**1**, 19692-10-5; **2**, 41316-14-7; **3a**, 4136-15-8; **3b**, 41316-16-9; **3c**, 41316-19-2; **3d**, 41316-17-0; **3e**, 52147-54-3; **4a**, 4233-33-4; **5a**, 52147-55-4; **5b**, 52147-56-5; **5c**, 52147-57-6; **5d**, 52147-58-7; **6**, 52147-59-8; **8**, 15971-63-8; **10**, 52147-60-1; **11a**, 52147-61-2; **11b**, 41316-20-5; **12**, 52147-62-3; **13**, 52147-63-4; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 2,3-dimethylbutadiene, 513-81-5; isoprene, 78-79-5; butadiene, 106-99-0; 4-phenylurazole, 4233-33-4; benzyl bromide, 100-39-0; methyl iodide, 74-88-4; allyl bromide, 106-95-6; *tert*-butyl bromide, 507-19-7; bicyclo[2.1.0]pentane, 185-94-4; cyclopentene, 142-29-0.

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Furazans and Furazan Oxides. V.[1] Tropono[4,5-*c*]-, Thieno[2,3-*c*]-, and Biphenyleno[2,3-*c*]furazan Oxides

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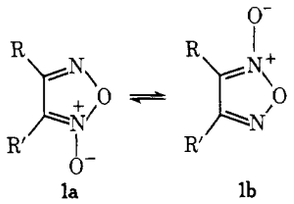
The three title furazan oxides were prepared, and the free energies of activation for their rearrangement were investigated. The relevance of these results to the question of the aromaticity of tropone, thiophene, and biphenylene is discussed. An important factor affecting the ease of the reaction appears to be the size of the ring to which the furazan oxide is fused.

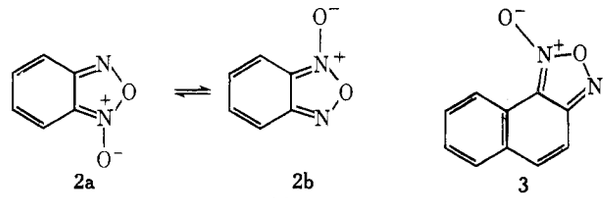
The striking difference (~19 kcal mol^{-1}) between the free energies of activation for the isomerization of a furazan oxide (furoxan[2]) (**1a** ⇌ **1b**) and a benzofurazan oxide (**2a** ⇌ **2b**) has led us to suppose that the reaction may provide a sensitive probe of, and an at least semiquantitative means of determining, the "aromaticity" associated with the ring to which the heterocyclic nucleus is fused. In earlier work,[3] the effect of naphtho[1,2] fusion (**3**) was found to be intermediate (ΔG^* ~19.5 kcal mol^{-1}) between that of benzo fusion (**2**) and "olefin fusion" (*i.e.*, the unfused system, **1**). However, interpretation of the results from polycyclic fused systems was not straightforward: allowance had to be made for changes in the aromaticity of the further fused ring as the one carrying the furoxan becomes more "benzenoid" upon opening of the heterocyclic ring. Nevertheless, we hoped that it might be possible to obtain a comparison between the aromaticities of naphthalene and biphenylene in this way. The problem does not arise when the furoxan is

anellated to a monocyclic ring, and therefore we decided also to examine the effect of fusion to tropone and thiophene.



1a 1b

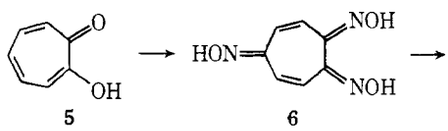
ΔG^* 33 kcal mol^{-1} [1,4]



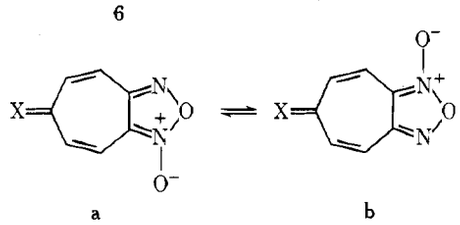
2a 2b 3

ΔG^* 14 kcal mol^{-1} [5]

6-Keto-6*H*-cyclohepta[*c*]furazan 1-Oxide (Tropono-[4,5-*c*]furoxan) (4). In the hope that light could be shed on the much-discussed[6] question of the aromaticity of tropone, we prepared tropono[4,5-*c*]furoxan (**4**). α-Tropolone (**5**) was converted into the known trioxime **6**, which was oxidized to the furazan oxide **7**. Removal of the remaining oxime group was difficult, but this was finally achieved using copper carbonate and formic acid.[7]

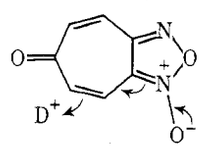


5 6



a b

4, X = O
7, X = NOH



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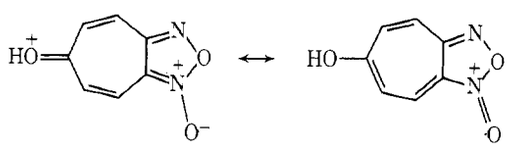


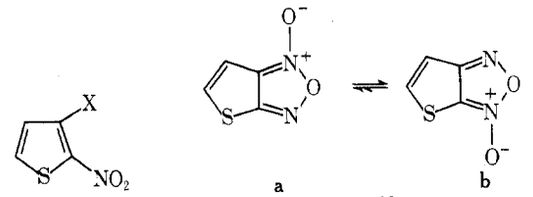
9

The mass spectrum of troponofuroxan (**4**) showed prominent peaks at P − 16 (–O) and P − 60 ($-N_2O_2$), as is frequently observed in furazan oxides,[8] and also at P − 28 (–CO) and P − 88 ($-CON_2O_2$).

The pmr spectrum of **4** showed two AB patterns (τ_a 2.32, τ_b 3.17, τ_c 2.665, τ_d 3.32; J_{ab}, J_{cd} = 12 Hz), with further long-range coupling (J_{bc} = 2 Hz).[9] No change in the spectrum was observed on heating: up to 150° the peaks were not noticeably broader than at room temperature. Assuming that the coalescence temperature is at least 40° above this, a lower limit of 24 kcal mol^{-1} can be placed on the free energy of activation for the reaction **4a** ⇌ **4b**.

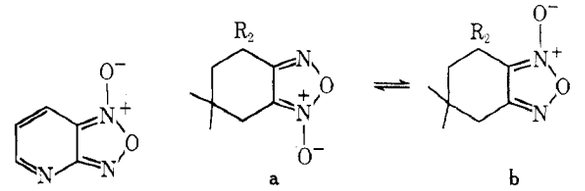
We attempted to exchange one of the protons in **4** for deuterium (*cf.* **8**), in order to follow the isomerization by conventional kinetic measurements. However, no exchange was observed on standing the furoxan with CF_3COOD/D_2SO_4 for several hours, or on heating it to 100° for 30 min. The immediate color change seen on adding D_2SO_4 suggested that the tropone oxygen atom was protonated (**9**); this probably served to prevent further reaction. No coalescence or exchange broadening effects were found in the nmr spectrum of **9**, up to 100°.

Thieno[2,3-*c*]furazan Oxide (10). A few furoxans fused to five-membered rings have been prepared; they are all to some extent unstable.[10] However, no compound containing an aromatic five-membered ring fused to a furoxan has yet been reported. We aimed to prepare the thieno-fused derivative (**10**), because the ease of its isomerization (**10a** ⇌ **10b**) might provide information on the "aromaticity" of thiophene, relative to benzene, from a source independent of other criteria which have been applied in the past (*e.g.*, from ring current,[11] bond localization from coupling constants[12] or from bond lengths,[13] etc.[14]).



11, X = Br
12, X = SPh
13, X = SO_2Ph
14, X = N_3
15, X = NH_2

a 10 b



16 a b

17, R_2 = O
18, R_2 = H,OAc

The replacement of the bromine by azide in 3-bromo-2-nitrothiophene (**11**) was effected by the sequence **11** → **12** → **13** → **14**, after attempts at direct replacement by azide ion in **11** had proved fruitless.[15] The azide **14** (the mass spectrum of which[9] showed significant differences from that of the furoxan: *cf.* ref 8b) was decomposed thermally, to give the furoxan **10**, in low yield. Other possible routes to **10**, *via* hypochlorite or phenyliodoso diacetate oxidation of the amine **15**, were still less successful, although the latter reagent did provide some furoxan. The amine was prepared by borohydride reduction of the azide **14**, after attempts directly to aminate the bromide **11** and the sulfone **13** had failed.

The furoxan **10**, characterized by its mass spectrum[9] and analytical data, showed in its pmr spectrum an AB pattern at room temperature, but the two isomers (**a** and **b**) gave separate signals at −45° (Figure 1). By comparison with benzofuroxans,[16,17] the shielding effect of the *N*-oxide group on an adjacent proton identifies the major isomer as **10a**; the equilibrium constant is 8 ± 1 at −45° ($\Delta G°$ 0.95 ± 0.07 kcal mol^{-1}). From the coalescence temperature for the fusion of signals H_a and $H_{a'}$ (−28 ± 10°), the free energy of activation ΔG^* for the isomerization **10b** → **10a** was determined[17] to be 12.3 ± 1 kcal mol^{-1}, the reverse reaction surmounting a barrier ~1 kcal higher.

The results therefore suggest, rather unexpectedly, that the tendency to form the transition state for the furoxan

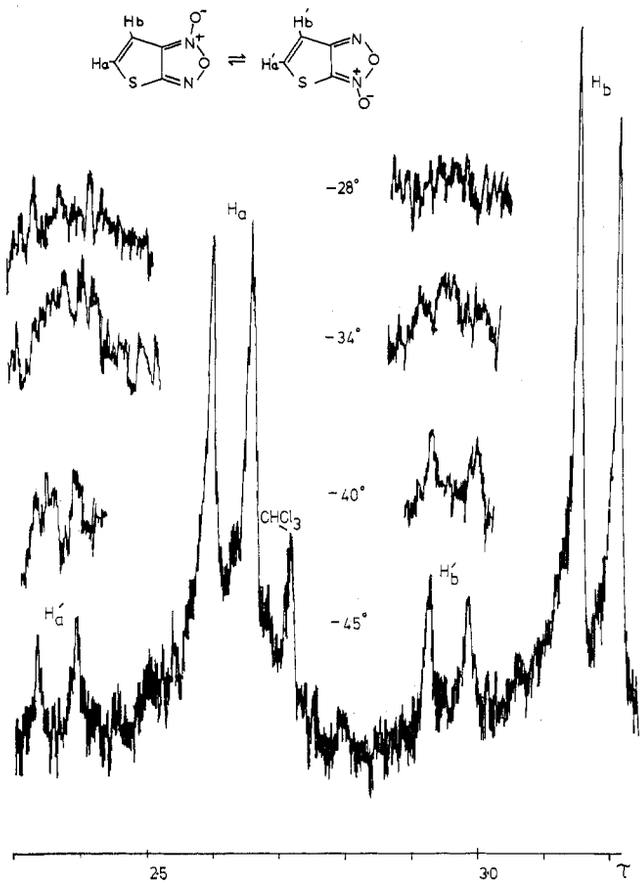


Figure 1. The pmr spectrum of thieno[2,3-*c*]furazan oxide (**10**) at various temperatures.

isomerization is greater in thieno[2,3-*c*]furoxan (**10**) than in benzofuroxan (**2**). It would, however, be unjustified to argue, on the strength of this, and in the face of a considerable body of evidence to the contrary, that the aromaticity of thiophene is greater than that of benzene. Two factors which might tend to lower the activation energy of **10**, by stabilizing 2,3-dinitrosothiophene, are electronic and ring-strain effects. The nitroso group is strongly electron withdrawing,[18] and the dinitrosothiophene would be expected to be stabilized as a result of the conjugation of these groups with the ring, which is generally accepted to be a better electron donor[19] than benzene. However, no evidence for the acceleration of benzofuroxan tautomerism by electron-donor substituents has been found in the past,[17] and furthermore pyrido[2,3-*c*]furoxan (**16**) and its derivatives isomerize at about the same rate as benzofuroxan,[20] despite the electron-withdrawing effect of the pyridine ring.

Ring strain provides a reasonable explanation for the observed results. We have already noted[10] that furoxans fused to five-membered rings show unusual properties, and even when fused to six-membered rings, as in the cases of compounds **17** and **18**,[21] the energy of activation for their isomerization (**a** ⇌ **b**) is slightly but significantly lower than that for unfused, provided that they are not amino conjugated, examples (**1**), by ~1 kcal mol^{-1}

A number of furoxans have been studied by X-ray crystallography,[22-25] and the "natural" bond angles in unfused compounds may be used to give an indication of whether or not fusion to another ring introduces strain, *tending* to widen the angle between the C=N bonds, and thus lengthen and weaken the O—N-2 bond. The published data on unfused furoxans give a mean value of 37° (± 2°) for this angle (α; see Figure 2b), which is close to

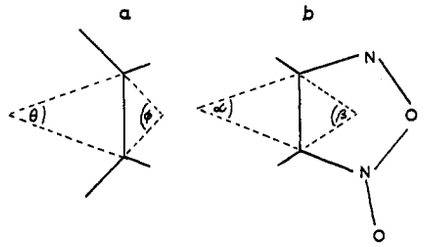


Figure 2. Bond angles in fused rings: $\theta = 360/n$; $\phi = 180(1 - 4/n)$; n = number of sides of a regular polygon.

that expected (36°) for the angle between nonadjacent sides of a regular pentagon. It is considerably smaller than the angle (θ; see Figure 2a) between radii of a regular hexagon (60°); indeed, for a regular n-gon θ falls to 37° only when n approaches 10.

The angle between the bonds to the 3 and 4 substituents of a furoxan (β in Figure 2b) is expected to be very susceptible to steric effects. For four substituted furoxans (the isomeric pairs of methyl *p*-bromophenyl[24] and methyl carbohydrazide[25] compounds) it is 80 ± 4°. This may be greater than that in the (unknown) unsubstituted compound, because of steric repulsion between substituents, but, accepting it as normal, it is comfortably satisfied by seven-membered ring fusion (ϕ = 77.1° when n = 7 in Figure 2a). These considerations suggest, therefore, that there is no appreciable extra strain involved in fusing a regular seven-membered ring to a furoxan, over that which the (substituted) five-membered ring itself contains. The angle ϕ in tropone (positions 4 and 5) is 76°, from X-ray diffraction data;[26] θ is 57° (nematic phase nmr measurements[27]).

For fusion to bond b of thiophene, the relevant angles θ and ϕ, derived from the microwave determination of the geometrical parameters by Bak, *et al.*,[28] are 72 and 44°. The former is considerably greater than α (37°) for furoxan: in drawing together the substituents on the thiophene ring to close the furoxan, ~35° of angle deformation has to be accommodated by the two bond angles interior to the furoxan ring at the fusion bond. This compares with 23° (60 − 37°) for benzo fusion. (X-ray diffraction data on benzofuroxans[23] indicate that these angles are the same, within a fairly wide margin of error, as in the unfused compounds.[22,24,25]) We consider that the extra bond angle strain in thieno[2,3-*c*]furoxan satisfactorily explains the anomalously low activation energy of isomerization of this compound.

Arising out of the above argument is the notion that benzofuroxan (**2**) may also be strained somewhat, and therefore the activation energy for the degenerate tautomerism of **4** would not have provided a reliable measure of the aromatic resonance stabilization energy of tropone, unless the effects of strain in **2** could be taken into account. Not wishing to become involved in the making of corrections of this kind, we therefore concentrated our attention upon the tautomerism of furoxans fused only to six-membered rings.

Biphenyleno[2,3-*c*]furazan Oxide (19). Introduction and Synthesis. Comparisons of the properties of biphenylene and naphthalene have been made on numerous occasions, since the early observations that, in contrast to naphthalene, bond orders, as revealed by chemical reactivity and bond lengths, indicated a greater degree of double-bond character between the 2 and 3 positions of biphenylene than between the 1 and 2—the "bond fixation" effect (see discussion in ref 29). This was satisfactorily explained using the Hückel MO theory.[30] For a quantitative comparison between the two systems, a distinction must be made between total delocalization energies, for the molecules as a whole, and the "local aromatic properties," in which the

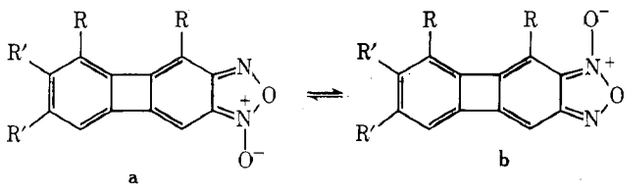
Table I
Bond Alternation and "Local Aromaticity" Comparisons

Compd	π-bond order,[a] larger/smaller	Aromaticity index[b]	Ortho coupling constants (Hz), larger/smaller[a,c]	Bond lengths (Å), longer/shorter[a,d]
Benzene	0.667/0.667 = 1.00	0.00	7.5/7.5 = 1.00	1.39/1.39 = 1.00
Naphthalene	0.725/0.603 = 1.20	1.803	8.2/6.9 = 1.19	1.415/1.364 = 1.037
Biphenylene	0.691/0.621 = 1.11	0.506	8.1/7.1 = 1.14	1.423/1.385 = 1.027

[a] Data relate only to the 1,2 and 2,3 bonds. [b] Defined in, and taken from, ref 31. [c] From ref 37, and G. Englert, P. Diehl, and W. Niederberger, *Z. Naturforsch. A*, **26,** 1829 (1971). [d] From ref 35, and E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Nature*, **173,** 75 (1954).

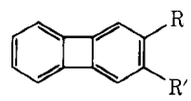
aromaticity associated with the individual rings of a molecule is assessed. The concept of local aromatic properties in polycyclic systems has been developed by Kruszewski,[31] who used the results of HMO theory, rather than any experimentally derived index of bond alternation, and classified biphenylene, together with naphthalene, as containing "moderately aromatic rings." Julg and François[13] have proposed an index of aromaticity based upon measurements of bond alternation, and for this the use of H–H coupling constants instead of bond orders (between which a linear relationship approximately obtains[32]) has been applied.[12] Bond alternation in fused benzene rings has recently been investigated in this way.[33] MO theory,[30,34] X-ray diffraction data,[35] and nmr coupling constant measurements[36,37] all agree in assigning to naphthalene a greater degree of bond alternation than to biphenylene, which according to these criteria has a higher aromaticity in its six-membered rings than has naphthalene (see Table I for relevant details).

For both naphthalene and biphenylene there are two possible ways of fusion of a furoxan ring—across the 1,2 and 2,3 bonds. While naphtho[1,2-*c*]furoxan (**3**) has been investigated,[3] naphtho[2,3-*c*]furoxan is unknown, and attempts to prepare it have failed.[3,38] For comparison with the known isomer, we set out to prepare biphenyleno[2,3-*c*]furoxan, and to determine the energy of activation for its (degenerate) isomerization (**19a** ⇌ **19b**). One substituted derivative, **20,** has been reported previously,[39] but it was not suitable for the present study.

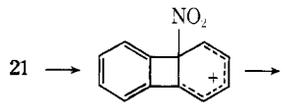


a **b**

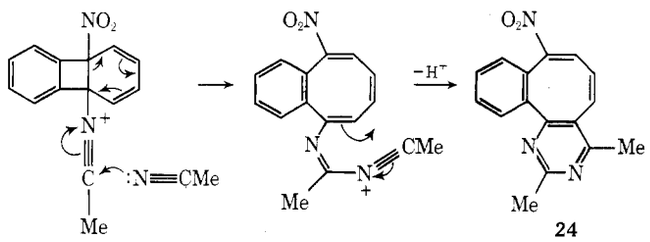
19, R = R′ = H
20, R = Me; R′ = OMe



21, R = R′ = H
22, R = NH_2; R′ = NO_2



23



24

Biphenylene (**21**) was nitrated,[40] and the 2-nitrobiphenylene was aminated[41] to give 2-amino-3-nitrobiphenylene (**22**). The nitro amine (**22**) was oxidized [$PhI(OAc)_2$][42] to the furoxan **19** in good yield.

The first two stages of the synthesis, however, both proceed in low yield. We therefore tried (unsuccessfully) to find an alternative route to 2-nitrobiphenylene. Attempted nitration ($C_5H_{11}ONO_2$) of 2-lithiobiphenylene (prepared from **21** by bromination[43] and metal–halogen exchange) gave biphenylene as the only identified product. The major product of nitration of biphenylene in acetic anhydride is 5-acetoxy-10-nitrobenzocyclooctene;[44] this presumably arises by addition of acetate ion to the biphenylene–nitronium ion adduct **23,** followed by ring opening. We hoped to reduce the importance of this reaction by reducing the nucleophilic power of the solvent, and therefore tried nitration with nitric acid in trifluoroacetic acid (TFA) and its anhydride, and TFA/dichloromethane (1:5). In no case was any nitrobiphenylene isolated from the reaction. With nitronium tetrafluoroborate in acetonitrile a yellow product was obtained, to which, on analytical and spectral evidence and a logical mechanism for its formation, we assign the fused pyrimidine structure **24.** Particularly revealing in the nmr was the ABX pattern from the protons on the eight-membered ring (τ_A 3.67, τ_B 3.38, τ_X 2.33; J_{AB} = 11.7 Hz, J_{AX} = 3 Hz, J_{BX} = 0.7 Hz).

Results and Discussion. The nmr spectrum of **19,** in CCl_4 at 34°, showed a 4 H singlet at τ 2.63 and two 1 H doublets (J = 1 Hz) at 3.195 and 2.925, for H-5–8, and H-4 and H-9, respectively. Heating (DMSO; sealed tube) resulted in (reversible) coalescence of the latter signals, with T_c 129 ± 4°. Application of the Gutowski–Holm approximation and Eyring's equation to the rate of inversion **19a** ⇌ **19b** so obtained[17] gives a value of 20.6 ± 1 kcal mol^{-1} for the free energy of activation ΔG^* at T_c. This is slightly *higher* than that obtained[3] for naphtho[1,2-*c*]furoxan (**3**). Since the evidence summarized in the introduction suggested that the individual rings of biphenylene displayed *less* bond alternation than those in naphthalene, this result is unexpected. There is not necessarily a linear correlation between the activation energy for tautomerism of a fused furoxan and either any measure of the "local aromaticity" of the ring to which it is fused, or (more simply) the order of the bond between the atoms carrying the nitroso groups in the intermediate (or transition state). However, the reversal in the order suggested by naive prediction is not easy to explain.

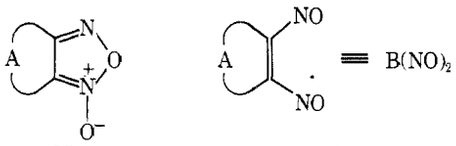
An alternative approach is to treat the delocalization energies of the heterocycle (**25**) and the dinitroso compound (**26**), in the following way. Consider the fused furoxan (**25**) to be built up from an alternant π-electron system A and the heterocyclic ring H. The delocalization energy of the fused system (**25**), DE_F, is $DE_A + DE_H + X$, where X is the increment resulting from the overlap of the two systems A and H. Similarly, the dinitroso compound (**26**) has

Table II
HMO π-Delocalization Energies[a]

Compd	DE_A	DE_B	$DE_B - DE_A$
2	0.47	2.00	1.53
3	2.42	3.68	1.26
19	3.15	4.51	1.35

[a] All figures, in units of β, are rounded off to second decimal place.[30,47,48]

delocalization energy $DE_D = DE_B + 2DE_{NO} + Y$, Y being the increase in delocalization energy produced by the addition of the two nitroso groups to the system B. If the transition state is approximately represented by **26**, then the difference in activation energies between two fused furoxan systems P and Q should be given by the difference between the delocalization energy differences ($DE_F - DE_D$) for the two systems, changes in σ-bonding energies, those due to strain,[45] etc., cancelling in the subtraction process. Furthermore, if we can set the contributions DE_H, DE_{NO}, X, and Y as equal between the systems,[46] then the difference in activation energies is given by $(DE_B - DE_A)_P - (DE_B - DE_A)_Q$. These quantities are readily accessible from simple Hückel MO calculations.[34,47,48]



25 **26**

The results from this approach were at first sight promising (Table II): the difference in activation energies between naphtho[1,2-*c*]furoxan (**3**) and benzofuroxan (**2**) is calculated to be 0.27β, equivalent[49] to ~5 kcal mol^{-1}, which is, within experimental error, just what is observed. Unfortunately, in the case of biphenyleno[2,3-*c*]furoxan (**19**), the calculated value is 1.6 kcal mol^{-1} (0.09β) *below* that of **3**; the value found is ~1 kcal *above*. Clearly, a more sophisticated approach[46,50] is necessary before the rationalization of the activation energies for isomerization of fused furoxans can be achieved. Until then, it does not seem likely that the reaction can be used to provide any useful quantitative information about aromaticity, "local" or otherwise.

Experimental Section

Melting points are uncorrected. Nmr spectra were of $CDCl_3$ solutions, taken on a Varian HA-100 instrument, with V4343 variable temperature probe attachment, unless otherwise specified. Ir spectra were of samples mulled with bromoform, unless otherwise stated. Mass spectra (70 eV ionizing potential) were measured on a Hitachi Perkin-Elmer RMU 21 instrument.

6-Hydroxyimino-6*H*-cyclohepta[*c*]furazan 1-Oxide (7). α-Tropolone[51] was converted by sodium nitrite in acetic acid into 5-nitrosotropolone[52] (cyclohepta-3,6-diene-1,2,5-trione 5-oxime). This (0.5 g) was heated under reflux 2 hr in ethanol (50 ml) with hydroxyammonium chloride (0.75 g). Removal of solvent left a dark red oil, which was dissolved in the minimum quantity of hot water and decanted from a small amount of undissolved tar. On cooling, the solution deposited buff prisms of the trioxime **6** (0.45 g, 82%), mp 206–207° (lit.[53] mp 204°). The trioxime (1.2 g) in aqueous NaOH (1 *N*, 50 ml) was stirred for 10 min with potassium ferricyanide (3 g in 20 ml of H_2O). The brown precipitate which formed was filtered off, dissolved in ether, dried ($MgSO_4$), and purified by chromatography on silica (eluant hexane–ethyl acetate, 2:1), giving the hydroxyiminofuroxan **7** as pale yellow prisms (0.4 g, 34%), mp 185–186° (sublimes), which, despite the sharp melting point, was probably a mixture of isomers: ir 3180–2740 (br), 1595, 1520, 1480, 1440, 1020 cm^{-1}; mass spectrum *m/e* (rel intensity) 179 (73), 163 (20), 149 (31), 119 (100).

Anal. Calcd for $C_9H_7N_3O_4$: C, 48.9; H, 3.2; N, 19.0. Found: C, 47.4; H, 3.1; N, 23.2.

In acetic anhydride the oxime **7** formed an acetate: mp 143–165° (from ethyl acetate–hexane); ir 1786, 1598, 1530, 1363 cm^{-1}. Both this compound and the oxime **7** gave complex nmr spectra in the region of τ 2.5–3.5, not analyzable as simple ABCD systems and suggesting the presence of geometrical isomers. The spectra were unchanged up to 130°.

Anal. Calcd for $C_9H_7N_3O_4$: C, 48.9; H, 3.2; N, 19.0. Found: C, 48.4; H, 3.5; N, 18.7.

6-Keto-6*H*-cyclohepta[*c*]furazan 1-Oxide (8). The oxime **7** (0.4 g) in formic acid (20 ml, 98%) was heated for 48 hr under reflux with cupric carbonate (1 g). Water (50 ml) was added, and the acid was neutralized with sodium hydrogen carbonate. The organic material was extracted into ethyl acetate, and the extract was washed with 1 *N* NaOH to remove unchanged oxime. The organic layer was dried ($MgSO_4$), concentrated, and filtered through a short column of alumina, eluting with ethyl acetate. The solvent was removed and the residue was recrystallized from hexane, giving the troponofuroxan **8** as pale yellow needles (0.12 g, 33%): mp 95–96°; ir (CCl_4) 1600 (vs), 1628, 1640 cm^{-1}; nmr (see text).

Anal. Calcd for $C_7H_4N_2O_3$: C, 51.2; H, 2.5; N, 17.0. Found: C, 51.0; H, 2.6; N, 16.9.

The following unsuccessful attempts were made to prepare **8** from its oxime **7**. (a) (*Cf.* ref 54). The oxime (50 mg) was heated in formalin (1 ml) and concentrated hydrochloric acid (1 ml) under reflux for 4 hr. (b) (*Cf.* ref 55). The oxime (50 mg) was heated under reflux for 3 days in ethanol (1 ml) and aqueous sodium hydrogen sulfite (1 ml, 40%). (c) (*Cf.* ref 56). The oxime (75 mg) in methanol (5 ml) was stirred for 10 min with thallium(III) nitrate (185 mg) in methanol (5 ml). Aqueous sulfuric acid (3 *N*, 20 ml) was added, and the solution was extracted with chloroform. The chloroform solution was dried ($MgSO_4$) and filtered through an alumina column. The oxime was recovered unchanged from processes a–c. (d) The oxime (88 mg) was converted into its tosylate (mp 202–204°) using *p*-toluenesulfonyl chloride in pyridine. The tosylate was heated in dioxane for 5 min at 65° with a large excess (~5 mol) of sodium borohydride. Tlc examination showed the tosylate to remain. A catalytic amount (~0.1 mol) of aluminum chloride was added, and heating was continued for 5 min. Addition of water and ether extraction gave unchanged tosylate.

3-Azido-2-nitrothiophene (14). 3-Bromo-2-nitrothiophene (**11**)[57] was converted by alkaline ethanolic benzenethiol into the 3-phenylthio compound **12**,[58] which was oxidized to the sulfone **13**,[59] forming cream-colored prisms, mp 140–141° (from $CHCl_3$–hexane (lit.[59] mp 143°). The sulfone (2 g) was stirred at 20° in dimethyl sulfoxide (50 ml) for 2.5 hr with sodium azide (0.6 g). Water (150 ml) was added, and the mixture was extracted with ether (3 × 50 ml). After drying ($MgSO_4$), the extracts were passed down a short (3 cm) alumina column. The eluate was concentrated and warmed, and hexane was added. The mixture was cooled to provide the azide as prisms (1.1 g, 87%): mp 79–81° dec; ir 2160, 2105, 1540, 1330 cm^{-1}; for mass spectrum see footnote 9. A satisfactory elemental analysis could not be obtained for this compound, owing to its ready decomposition.

3-Amino-2-nitrothiophene (15). Sodium borohydride (0.5 g) in methanol (20 ml) was added to the azide **14** (0.68 g) in methanol (30 ml), cooling in an ice bath to maintain the temperature below 20°. After the initially vigorous reaction had ceased (20 min) the methanol was removed *in vacuo*, water (10 ml) was added, and the acidity was adjusted to pH 7 with dilute HCl. Ether extraction (3 × 20 ml), drying ($MgSO_4$), and removal of solvent from the extract gave the amine as yellow prisms (0.52 g, 90%) (from ethyl acetate–hexane), mp 59–60° (lit.[60] mp 58.5–60°).

Thieno[2,3-*c*]furazan Oxide (10). A. From the Azide 14. The azide (0.22 g) was heated to reflux for 30 min in acetic acid (25 ml). Saturated aqueous NaCl (150 ml) was added to the cooled solution, and the mixture was extracted with ether (3 × 25 ml). The combined extracts were washed once with brine and twice with aqueous sodium hydrogen carbonate, then dried ($MgSO_4$), and filtered through alumina. The ether was removed, and the yellow residue of furoxan **10** was recrystallized from hexane, giving pale yellow needles (0.08 g, 45%): mp 101–102° (sublimes); ir 3100, 1635, 1500, 1470, 1410 cm^{-1}; nmr τ_A 2.6, τ_B 3.15 (J_{AB} = 6 Hz) at 30°; for low temperature spectrum see Figure 1; for mass spectrum see footnote 9.

Anal. Calcd for $C_4H_2N_2O_2S$: C, 33.8; H, 1.4; N, 19.7. Found: C, 33.9; H, 1.5; N, 19.8.

More concentrated azide solutions, treated as above, resulted in lower yields, while no furoxan was isolated from thermolysis in toluene.

B. From the Amine 15. The amine (0.09 g) was allowed to stand

for 24 hr in chloroform (50 ml) with phenyliodoso diacetate (1.0 g), followed by heating to 40° for 1 hr. The solvent was removed, ethyl acetate (10 ml) was added, and the solution was passed through a short alumina column. Removal of solvent gave the crude furoxan **10** (19 mg, 26%), mp 96–99°.

The furoxan **10** was reduced to a complex mixture of products by trimethyl phosphite in ether at 0°, but we were not able to isolate any of the expected furazan from this.

2-Nitrobiphenylene. Biphenylene[61] (3.0 g) was nitrated according to the method of Baker, *et al.*[40] The product was purified by chromatography on silica, giving yellow needles: mp 105–6° (lit.[40] mp 105–106.5°); 0.45 g, 12%.

In an attempt to improve the yield, samples of biphenylene were stirred for 1 hr at 0° with nitric acid (*d* 1.42, 1.2 equiv.) in (a) trifluoroacetic acid, (b) trifluoroacetic anhydride, and (c) dichloromethane–trifluoroacetic acid (5:1). In each case water was next added and the mixture was extracted with ethyl acetate. A tlc examination showed the presence of several components less mobile than biphenylene, but none of the 2-nitro compound was detected.

Biphenylene was converted into 2-bromobiphenylene, using bromine and thallic acetate.[43] 2-Bromobiphenylene (0.53 g) in ether (100 ml) was treated at −50° with *n*-butyllithium in hexane (4 ml, 15%). The solution was allowed to reach room temperature, and, after again cooling to −50°, dry isoamyl nitrate was added and the solution was stirred for 1 hr, the temperature warming to 10°. The mixture was allowed to stand overnight and was then washed with water. Much tarry material was deposited. Examination of the solution and tars by tlc revealed the presence of biphenylene and at least three other components, but no 2-nitrobiphenylene.

2-Amino-3-nitrobiphenylene(22). 2-Nitrobiphenylene (0.45 g) was aminated, using hydroxylamine hydrochloride and potassium hydroxide in methanol.[41] The product **22** (0.19 g, 38%) and unchanged nitrobiphenylene were separated by chromatography on alumina (benzene–chloroform).

Biphenyleno[2,3-*c*]furazan Oxide (19). Iodosobenzenediacetate (0.5 g) in benzene (20 ml) was added to a suspension of 2-amino-3-nitrobiphenylene(0.19 g) in benzene (50 ml), and the mixture was stirred for 15 hr. Removal of solvent *in vacuo* and chromatography on silica (hexane–ethyl acetate, 6:1) gave the furazan oxide **19** as light brown prisms (0.13 g, 70%): mp 198–200°; ir (CCl_4 solution) 1613, 1495, 1456 cm^{-1}; for nmr see text; mass spectrum *m/e* (rel intensity) 210 (P^+, 41%), 194 (40), 178 (18), 164 (18), 152 (22), 151(25), 150 (100).

Anal. Calcd for $C_{12}H_6N_2O_2$: C, 68.6; H, 2.9; N, 13.1. Found: C, 68.6; H, 3.0; N, 13.1.

2,4-Dimethyl-8-nitrobenzocycloocteno[5,6-*d*]pyrimidine (24). Nitronium tetrafluoroborate[62] (1.22 g) in acetonitrile (80 ml, from P_2O_5) was added over 1 hr to a stirred solution of biphenylene (1.2 g) in dry acetonitrile (150 ml) at 0° under N_2. After 1 hr at room temperature the solvent was removed, leaving a green solid which was shaken with saturated aqueous Na_2CO_3 (50 ml) and then with ethyl acetate (50 ml). The bright red organic layer was dried ($MgSO_4$) and filtered through alumina. Concentration and cooling gave the pyrimidine **24** as yellow prisms (0.94 g, 43%): mp 211°; ir 2960, 1550–1530 (br), 1525, 1430, 1380, 1330 cm^{-1}; nmr ($CDCl_3$) τ 7.55 (3 H) and 7.27 (3 H, 2 CH_3), 3.85–3.25 (m, 2 H, H_A, H_B), 2.9–2.5 (4 H, H-9–12), 2.4–2.3 (m, 1 H, H_X) (see text); mass spectrum *m/e* (rel intensity) 279 (P^+, 5%), 233 (58), 192 (100), 151 (82), 150 (23).

Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.8; H, 4.7; N, 15.0. Found: C, 68.9; H, 4.7; N, 14.7.

The pyrimidine **24** gave a crystalline hydrochloride [mp 211° dec; ir (Nujol mull) 2500–2200, 1950, 1630, 1525, 1340 cm^{-1}] by extraction of **24** from ethyl acetate into 10% aqueous hydrochloric acid and precipitation of the salt with acetone.

Attempts to contract the cyclooctene ring with base (*cf.* Barton and Whitaker[44]) led to recovery of starting material. The pyrimidine **24** (0.1 g) in methanol (15 ml) was stirred with potassium carbonate (0.5 g) for 4 days. Removal of methanol and addition of water gave a clear yellow solution from which nothing was extracted by ethyl acetate. Neutralization of the alkali led to recovery of the pyrimidine, which therefore appears to function as an acid by reversible addition of hydroxide (or methoxide) to the nitroalkene part of the molecule. More forcing conditions (reflux with alcoholic KOH) led to decomposition, but to no identified products.

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Supplementary Material Available. Diagrams of the nmr spectra of compound **4** and the mass spectra of compounds **10** and **14**, and HMO data (including polarizabilities) of 1,2-dimethylenebenzocyclobutene, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-2956.

Registry No.—**4**, 52003-13-1; **6**, 52003-14-2; **7**, 52003-15-3; **7** acetate, 52003-16-4; **10**, 52003-17-5; **11**, 24430-27-1; **12**, 52003-18-6; **13**, 33786-80-0; **14**, 52003-19-7; **15**, 52003-20-0; **19**, 52003-21-1; **22**, 18798-45-3; **24**, 52003-22-2; **24** HCl, 52003-23-3; 5-nitrosotropolone, 52003-24-4; 2-nitrobiphenylene, 18931-53-8; biphenylene, 259-79-0; iodosobenzenediacetate, 3240-34-4; 1,2-dimethylenebenzocyclobutene, 20265-84-3.

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(45) We are here dealing only with furoxans fused to six-membered rings.
(46) (a) A referee, quite rightly, points out that this requires justification. DE_H and DE_{NO} are equal by definition. *X* and *Y* we had at first supposed would be equal because the fragments A and B are both alternant hydrocarbon systems, with, therefore, overall charge density of zero on each atom. For a rather more rigorous argument we extend the method of Brown[46b] to the two connections between A and H, and B and the NO groups. This leads to the expression

$$X = -[0.811(\sqrt{\lambda_a\lambda_h} + \sqrt{\lambda_{a'}\lambda_{h'}}) + 0.124]\beta$$

for the furoxan **25**, where λ's are the "self-atom polarisabilities" (also denoted by P, and π_{rr}) of the atoms A and H connected by the fusion. For **26**

$$Y = -[0.811\sqrt{\lambda_{NO}}(\sqrt{\lambda_b} + \sqrt{\lambda_{b'}}) + 0.124]\beta$$

taking λ's as positive. *Y* for *o*-dinitrosobenzene, 1,2-dinitrosonaphthalene, and 2,3-dinitrosobiphenylene is

$$-(k\sqrt{\lambda_{NO}} + 0.124)\beta$$

where *k* is 1.024, 1.056, and 1.056, respectively. For any reasonable value of λ_{NO}, the difference between these *Y* terms is very small—less than 0.5 kcal. *X* can be simplified, if we adopt a mean value $\lambda_{\bar{h}}$ for the polarisability at the heterocyclic ring, to

$$-[0.811\sqrt{\lambda_{\bar{h}}}(\sqrt{\lambda_a} + \sqrt{\lambda_{a'}}) + 0.124]\beta$$

The polarizabilities relevant to the biphenylenofuroxan case (A is 7,8-dimethylenebicyclo[4.2.0]octa-1,3,5-triene or 1,2-dimethylenebenzocyclobutene) are not available in ref 47 and are published as material supplementary to this paper.[9] *X* for furoxans **2**, **3**, and **19** is

$$-(k\sqrt{\lambda_{\bar{h}}} + 0.124)\beta$$

where *k* is 1.283, 1.159, and 1.300, respectively. The differences between *X*'s are not insignificant here: a correction (of *ca.* −2 kcal.) reducing $DE_B - DE_A$ for compound **3**, compared with **2** and **19**, should be made. This brings the calculated result for **3** more into line with the observed comparison between **3** and **19**, but now the comparison between **2** and **3** is upset. (b) R. D. Brown, *Aust. J. Sci. Res.*, **5A**, 339 (1952).
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(50) A further step (*cf.* also footnote 46) in this direction was suggested by the referee, who points out that it is incorrect, in biphenylene, to take all the resonance integrals across bonds as equal, the bonds joining the six-membered rings being so much longer than the rest. A small adjustment (to 0.8β) alters the total π energy by 0.187β (3.4 kcal) in the desired direction. However, it seems unreasonable not to introduce a similar correction to the fragment A (1,2-dimethylenebenzocyclobutene), and we find that the total π energy of this system is more sensitive to adjustment of the integrals of the corresponding bonds (π energy raised by 0.247β on reducing integral to 0.8β). This more than cancels out the adjustment made to the intermediate (**26**). We observe that, for both biphenylene and dimethylenebenzocyclobutene, as the resonance integral assigned to the long bonds is increased from 0 (separated systems) through $n\beta$ to 1β, the graph of π energy *vs.* *n* describes a parabolic curve between energies E_0 and E_1 (for 0β and 1β) of form

$$(E_n - E_0) = \sqrt{n}(E_1 - E_0)$$

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