Anal. Calcd. for $C_{16}H_{11}NO_2$: C, 77.1; H, 4.4; N, 5.6. Found: C, 77.3; H, 4.5; N, 5.6.

The forerun and residue containing 2,2'-dinitrobiphenyl and 1,1'-binaphthyl, respectively, have not been investigated.

1-(2-Aminophenyl)naphthalene (I).—The reduction of the preceding compound caused unexpected difficulties. Tin or titanous chloride in concentrated hydrochloric acid, as well as platinum–charcoal or palladium–charcoal in alcohol with hydrogen, left the nitro compound unaffected; and stannous chloride in concentrated hydrochloric acid, hydrazine hydrochloride with Raney nickel or palladium–charcoal, or hydrogen activated with palladium–charcoal in ethyl acetate or in ethanol containing some hydrochloric acid led to resinous products.

When 0.5 g. of 1-(2-nitrophenyl)naphthalene was hydrogenated in 50 ml. of ethanol containing a few drops of 60% *perchloric acid*, in the presence of 0.1 g. of palladium–charcoal (10%), the reaction was complete in 3 hr., and the amino compound, m.p. 62°, was obtained in 82% yield (lit.[3] m.p. 65°, softening at 61°).

Anal. Calcd. for $C_{16}H_{13}N$: C, 87.7; H, 5.9; N, 6.4. Found: C, 87.7; H, 5.9; N, 6.1.

9-Aminofluoranthene (II).—A solution of 3.12 g. of boron trichloride in 100 ml. of benzene was added, slowly and with stirring, to a solution of 4.5 g. of I in 120 ml. of benzene. The mixture was refluxed for 5 hr. and evaporated *in vacuo*, and the dry residue was heated for 3 hr. at 120° with 0.3 g. of finely powdered aluminum chloride. The product (yield 25%) was extracted repeatedly with anhydrous ether and the concentrated solution was chromatographed on silica. Platelets of m.p. 272° were obtained with λ_{max}^{EtOH} 262 mμ (log ϵ 4.70), 283 (3.99), 288 (4.30), 294 (3.80), 326 (4.17), 342 (3.63), and 358 (3.77), while we found for fluoranthene 277 (4.51), 283 (4.39), 289 (4.68), 310 (3.64), 326 (3.88), 344 (3.98), and 362 (3.99).

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.5; H, 5.1; N, 6.4. Found: C, 88.3; H, 5.5; N, 6.4.

Diazotization of the product and coupling with an alkaline solution of 2-naphthol gave an azo dye.

Fluoranthene.—A solution of 120 mg. of II in 1 ml. of concentrated hydrochloric acid was diazotized at 5° with 90 mg. of sodium nitrite. The solution was added at 10–15° to a solution of 1.3 g. of anhydrous cupric sulfate in 10 ml. of 32% hypophosphorous acid. After addition of 15 ml. of ethanol, the mixture was brought to a temperature of 55°, cooled, and extracted with ether. The concentrated solution was chromatographed on silica and gave one single compound of m.p. 110°, which was identified by analysis and mixture melting point as fluoranthene.

Anal. Calcd. for $C_{16}H_{10}$: C, 95.0; H, 5.0. Found: C, 94.7; H, 5.2.

7-Methyl-1-tetralone (IV) and 3,4,3',4-tetrahydro-7,7'-dimethyl-1,1'-binaphthyl (VIII), m.p. 115° (from ethanol), were prepared according to Newman[1] who reported a melting point of 110.0–11.6°. The hydrocarbon had λ_{max}^{EtOH} 255 mμ (log ϵ 4.30).

7,7'-Dimethyl-1,1'-binaphthyl (III).—A mixture of 2 g. of VIII and 0.2 g. of palladium–charcoal (10%) was heated for 3 hr. at 240° and for 2 hr. at 300–320°. The product was extracted with benzene, the solution was evaporated, and the solid residue was recrystallized from ethanol. The hydrocarbon (1.8 g., 90%) formed colorless needles of m.p. 164–165°, λ_{max}^{EtOH} 287 mμ (log ϵ 4.09) and 296 (4.09).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.5; H, 6.5.

2,3,7,8-Tetrahydro-6,11-dimethylbenzo[j]fluoranthene (IX).—A mixture of 21 g. of IV in 150 ml. of absolute ethanol and 100 ml. of dry benzene, 6 g. of aluminum foil cut to small pieces, and 0.5 g. of mercuric chloride was refluxed for 18 hr., acidified with dilute hydrochloric acid, and extracted with benzene. The organic layer was washed with 10% hydrochloric acid and a saturated solution of sodium chloride, and concentrated *without* washing with water or drying. The residue was refluxed for 3 hr. with 100 ml. of glacial acetic acid and the acid was removed *in vacuo*. Recrystallization of the residue from ethanol gave crystals of m.p. 118–119°, which depressed the melting point of VIII considerably: λ_{max}^{EtOH} 318 mμ (log ϵ 4.38) and 334 (4.28).

Anal. Calcd. for $C_{22}H_{20}$: C, 92.9; H, 7.1. Found: C, 92.6; H, 7.2.

6,11-Dimethylbenzo[j]fluoranthene (VI).—A mixture of 5 g. of IX and 0.5 g. of palladium–charcoal (10%) was heated at 240° for 3 hr. and at 300–320° for 2 hr. Extraction with benzene gave a solution which exhibited a weak, green fluorescence. The residue of the extract was a yellow compound (4.5 g., 95%) which was chromatographed on neutral alumina (benzene as

eluent) and recrystallized from ethanol, m.p. 173–174°. The absorption spectrum (in ethanol) showed the following bands: 244 mμ (log ϵ 4.78), 268 (infl.), 280 (4.23), 291 (3.58), 317 (4.25), 339 (4.00), 370 (3.58), and 390 (3.58).

Anal. Calcd. for $C_{22}H_{16}$: C, 94.3; H, 5.7. Found: C, 94.5; H, 5.9.

Some Nitronium Tetrafluoborate Nitrations

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In connection with other work in our laboratories we have had occasion to examine the competitive rates of nitration of several aromatic compounds with nitronium tetrafluoborate.[1] The nitrations were carried out at room temperature by adding dropwise 0.30 ml. of a 0.67 *M* solution of nitronium tetrafluoborate in tetramethylenesulfone to a solution containing 100 μl. of each of the aromatic compounds dissolved in 20 ml. of tetramethylene sulfone, while maintaining rapid stirring. The solutions were quenched with water and extracted with ether. The ether was washed with water, and dried; the ether was removed on the steam bath. The products were analyzed by gas chromatography on a 12 ft. $\times$ 0.25 in. o.d. column of DC-710 silicone fluid on firebrick (2:10) at a 200° temperature.

The relative rate constants obtained from the analyses, assuming the reaction to be first order in aromatic, are reported in Table I.

Table I
Competitive Nitrations with Nitronium Tetrafluoborate

Run	Rate ratio	Binary[a] value	Mixture[b] value	Lit.[c] value
1	Toluene–benzene	1.68	2.60	1.67
		1.74		
2	Benzene–chlorobenzene	7.6	3.32	7.1
3	Toluene–chlorobenzene	11.2	8.44	(11.8)
4	Benzene–fluorobenzene	1.89	1.50	2.22
		2.08		
5	Fluorobenzene–chlorobenzene	3.20	2.22	(3.21)
6	Chlorobenzene–bromobenzene	1.08		(1.17)
7	Toluene–fluorobenzene	6.72	3.80	(3.71)

[a] Nitration of a mixture of the two aromatics whose rate ratios are given. [b] Nitration of a mixture of benzene, toluene, fluorobenzene, and chlorobenzene. [c] See ref. 1; values in parentheses are calculated from the rates relative to benzene.

The close agreement of the values which we have obtained for binary mixtures, with the exception of fluorobenzene *vs.* toluene, with those reported by Olah[1] is in contrast with the values obtained from the four-component system.

In every case studied, however, the isomer distributions of the nitrated aromatics are in agreement with the values reported by Olah. With toluene, for example, we obtain *ortho–meta–para* ratios of 63:3:34 in close agreement with Olah's ratios of 65:3:32.

(1) G. A. Olah, *et al.*, *J. Am. Chem. Soc.*, **83**, 4564, 4571, 4581 (1961).

We have also studied the isotope effect on these reactions by competitively nitrating mixtures of bromobenzene and chlorobenzene, bromobenzene and p-chlorobenzene-d (88.2%), and bromobenzene and m-chlorobenzene-d (91%). The results are shown in Table II.

TABLE II

ISOTOPE EFFECTS ON THE NITRATION OF CHLOROBENZENE
WITH NITRONIUM TETRAFLUOBORATE IN
TETRAMETHYLENESULFONE SOLUTION AT 25.0°

Rate ratio	Value
p-Chlorobenzene-d–chlorobenzene[a]	1.05 ± 0.03[b]
(para–ortho)$_{p-D}$–(para–ortho)$_{p-H}$	1.06 ± 0.03[b]
m-Chlorobenzene-d–chlorobenzene	1.00 ± 0.02[b]
(para–ortho)$_{m-D}$–(para–ortho)$_{m-H}$	1.00 ± 0.03[b]

[a] Values are corrected for deuterium content. [b] The error reported is the maximum error found in five separate parallel determinations.

The isotope effects reported here are smaller than those reported for fluorobenzene and toluene nitrations.[1]

Since our data indicate that these reactions may not be well behaved kinetically, and since our primary interests are not in this field, we are discontinuing our investigations of these systems.
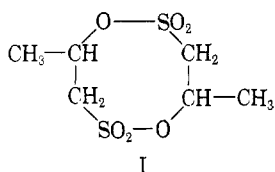

Conformational Analysis of a Disultone

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In a previous paper[2] the identification of 4,8-dimethyl-1,5-dioxa-2,6-dithiacyclooctane 2,2,6,6-tetraoxide (I) from the reaction of 1-propanol with sulfuryl


I

chloride was reported. The assignment of structure was based on chemical shifts in n.m.r. spectra and was confirmed by chemical degradation. It was observed that diastereomeric configurations are possible for I.

Although the utility of n.m.r. spectroscopy in conformational analysis of cyclic systems is well recognized, eight-membered rings have received scant attention.[3] Previous papers on this particular ring size have involved theoretical calculations, dipole moments, infrared and Raman spectra, and equilibration methods. It has been concluded that the preferred conformation of cyclooctane and its derivatives is a stretched crown.[4]

In our earlier work, the n.m.r. spectrum of the disultone (I) was discussed in terms of chemical shifts, which

(1) To whom inquiries should be addressed at Williams College.
(2) J. H. Markgraf, B. A. Hess, Jr., C. W. Nichols, and R. W. King, J. Org. Chem., 29, 1499 (1964).
(3) F. A. L. Anet and J. S. Hartman, J. Am. Chem. Soc., 85, 1204 (1963).
(4) N. L. Allinger, S. P. Jindal, and M. A. DaRooge [J. Org. Chem., 27, 4290 (1962)] critically review the literature relevant to such a conclusion.

permitted differentiation between structural isomers. In that case coupling between protons was not germane to the identification of isomers. With the correct structure of the disultone established, it was of interest to consider the conformation of I. The spin-decoupling method permitted the protons to be analyzed as an ABX system, giving $J_{AB} = 14.8$ c.p.s., $J_{AX} = \pm 1.3$ c.p.s., and $J_{BX} = \pm 9.5$ c.p.s. Regarding the coupling constants, J_{BX} is fairly large and indicates that one methylene proton and the methine proton are anti most of the time. The J_{AX} value is consistent with a dihedral angle of about 60°.[5] It thus seems that the disultone shows a strong preference for one conformation. That eight-membered rings exist predominantly in one conformation has been concluded by others.[4,6] Such an interpretation with respect to the anti relationship of the methine and methylene protons is consistent with the chemical degradations of I reported previously. It was established that hydride ion effected a facile E2 elimination to produce derivatives of trans-1-propene-1-sulfonic acid.[2] It is known that such concerted, bimolecular eliminations proceed most readily when the atoms to be eliminated, hydrogen and sulfonate in the present case, are anti.[7] This favorable conformation for the elimination process is a corollary of the methine–methylene arrangement mentioned above. These relationships are represented in the Newman projection (II) along the C-5–C-4 bond.

II
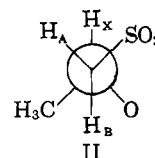
The question of the configuration of I remains unresolved; the methyl groups may be cis or trans. From Dreiding models it is evident that, when the preferred conformation (II) about the C-3–C-4 bond is satisfied, then the most reasonable molecular conformations (in terms of transannular repulsions and dihedral angles) are a stretched crown (III) for the cis isomer and a skewed chair[9] (IV) for the trans isomer. In both cases the methyl groups can be in comfortable "equa-

III   IV
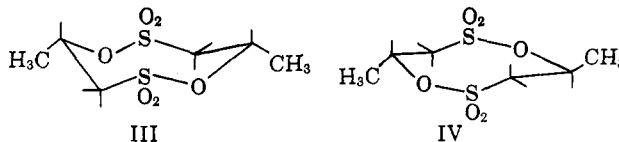
torial" positions. Although the cis isomer (III) is analogous to the preferred stretched-crown conformation for cyclooctane and derivatives,[4] it is not possible to infer the more stable configuration of the disultone

(5) M. Karplus, J. Chem. Phys., 30, 11 (1959).
(6) (a) N. L. Allinger and S.-E. Hu, J. Am. Chem. Soc., 83, 1664 (1961); (b) H. E. Bellis and E. J. Slowinski, Jr., Spectrochim. Acta, 15, 1103 (1959); (c) G. Chiurdoglu, T. Doehaerd, and B. Tursch, Chem. Ind. (London), 1453 (1959); (d) R. Kolinski, H. Piotrowska, and T. Urbanski, J. Chem. Soc., 2319 (1958).
(7) It is recognized, however, that ground-state conformations cannot necessarily be inferred from the products; cf. Eliel's discussion of the Curtin–Hammett principle.[8]
(8) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 149–152.
(9) R. Pauncz and D. Ginsburg, Tetrahedron, 9, 40 (1960).