Tetrahedron, 1963, Vol. 19, pp. 2111 to 2121. Pergamon Press Ltd. Printed in Northern Ireland

THE CONFORMATIONS OF 1,2-ACENAPHTHENE DERIVATIVES AND STERIC INTERACTION OF CONTIGUOUS NITROXY GROUPS[1]

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(*Received* 24 *June* 1963)

Abstract—Inter-oxygen distances and conformational flexibility were estimated for *cis*- and *trans*-1,2-acenaphthenediol from X-ray data, intramolecular hydrogen bonding, the kinetics of glycol cleavage, and cyclization experiments. The optical and NMR spectra of the isomeric dinitrate esters and related compounds in solution showed significant differences. The symmetric and antisymmetric stretching bands of the nitroxy group occurred at 1276 ± 2 cm^{-1} and 1639 ± 7 cm^{-1} respectively in the *trans*-dinitrate and in ethyl and benzyl nitrates and were shifted to higher frequencies by 9 cm^{-1} and 16 cm^{-1} respectively in the *cis*-dinitrate. The analogy to similar effects observed in cyclic 1,2-diketones, α-haloketones, and *o*-halonitrobenzenes suggested intramolecular interaction of the contiguous nitroxy groups.

The reaction of the dinitrates with pyridine at 25° was pseudo first-order and the ratio k_{trans}/k_{cis} of 6·5 was consistent with an Eco mechanism involving nitroxy group interaction in the *cis* isomer.

STEREOSELECTIVE nucleophilic attack on one of two or more secondary nitroxy groups has been observed in both cyclic and acyclic polynitrates.[2–8] Anhydrous pyridine, for example, caused preferential cleavage of one O—NO_2 bond in fully-nitrated penitols,[6] hexitols,[2,3] and dianhydrohexitols[7] as shown by retention of configuration at asymmetric centers[2,3] and by differences in reaction rates for diastereoisomers.[3,6,7] Intramolecular interaction between contiguous nitroxy groups or between nitroxy groups and neighbouring oxygen atoms was proposed as the steric factor in these reactions.[7] A similar interaction would be a plausible cause of the restricted rotation[12,13,14] and selective reduction observed in glycerol trinitrate[9,11] and the stepwise denitration of pentaerythritol tetranitrate by hydrazine.[10] Hetman recently suggested a structure for glycerol trinitrate in the presence of pyridine in which the nitroxy

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groups were linked by bonds which appeared to be analogous to those formed between the *ortho* nitroso groups in benzofurazan oxide.[15]

In the present work *cis*- and *trans*-1,2-*O*-substituted acenaphthene compounds (Table 1) were synthesized as models of polyol derivatives in which the intramolecular separation of the oxy groups was defined within narrow limits by the molecular conformations. The degree of conformational flexibility in these molecules was estimated from X-ray[16] and spectral data and from oxidation and cyclization experiments. The solution spectra and rates of reaction with pyridine of the isomeric dinitrate esters were then examined for evidence of steric effects.

EXPERIMENTAL

Optical spectra were recorded with Cary Model 14 and Perkin Elmer No. 21 spectrophotometers and PMR spectra with a Varian A60 instrument with tetramethyl silane as reference. M.p. were corrected against known standards.

Materials. Oxidation of pure acenaphthene (I; Table 1) with sodium dichromate in acetic acid[17] yielded crude 1,2-acenaphthenedione (acenaphthenequinone; II), m.p. 259–260°. The IR spectrum of this product (KBr) showed an absorption band at 1770 cm^{-1} which was also present in the spectra of a commercial sample of the quinone, m.p. 265–270° and of the solid impurity, m.p. 247–253°, removed from these samples by exhausting ether extraction. This band was not present, however, in the spectrum of a chromatographically homogeneous specimen of II prepared from ether-extracted material by recrystallization to a constant m.p. of 273–274° from glacial acetic acid (Found: C, 78·9; H, 3·41. Calc. for $C_{12}H_6O_2$: C, 79·1; H, 3·20%).

Reduction of II with $LiAlH_4$[18] gave an 89% yield of the *cis*- and *trans*-1,2-acenaphthenediols (III and IV) which were separated readily by fractional crystallization from methanol. (Found: (III) C, 77·1; H, 5·44; (IV) C, 77·2; H, 5·34. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·41%). The ester derivatives described in Table 1 were prepared and characterized by conventional techniques. The pure dinitrates were separated from nitroaromatic isomers by chromatography on acid-washed alumina[7] and were recrystallized from methanol. Yields: *cis*-dinitrate, 40·7%; *trans*-dinitrate, 29·8%. Hydrogenation of the dinitrates (100 mg; MeOH suspension over Pd-C)[8] followed by recrystallization from methanol gave the corresponding diols in pure form (III, 25%; IV, 39%). Reduction of the dinitrates with $LiAlH_4$ or $NaBH_4$[19] yielded only traces of III and IV.

The *O*-isopropylidene derivative of III[20] was obtained according to Method A of Christian *et al.*[21] in 36% yield after 22 hr. (Found: C, 78·9; H, 6·34. Calc. for $C_{15}H_{14}O_2$: C, 78·9; H, 6·18%). In essentially the same conditions 45% of IV was recovered unchanged after 77 hr and after 1250 hr no *trans*-diol could be detected in the reaction mixture which now contained 0·3% of the *cis*-diol (III) isolated by chromatography and identified through the IR spectrum and mixed m.p. (212·5–214·5°). Treatment of III (100 mg) dissolved in pyridine (20 ml) with an excess of dry phosgene[22] for 36 hr at room temp and recrystallization from benzene gave the *cyclic carbonate* (44·4%). (Found: C, 73·5; H, 4·01. $C_{13}H_8O_3$ requires: C, 73·6; H, 3·79%). Under the same conditions IV yielded a dark viscous oil (58·5 mg) which contained at least 4 compounds none of which resembled the *cis*-carbonate in R_f value or UV spectrum. The *cis*-carbonate (12·5 mg) in acetone (1 ml) treated with 0·2N methanolic barium hydroxide solution (1·5 ml) gave the corresponding diol (III) identified by paper chromatography and m.p. (205–207°). A suspension of III (186 mg) in benzaldehyde (2·5 ml) saturated with dry HCl was shaken for 19 hr, cooled, neutralized with pyridine and diluted with water to give 431·5 mg of crude *O-benzylidene derivative* which was

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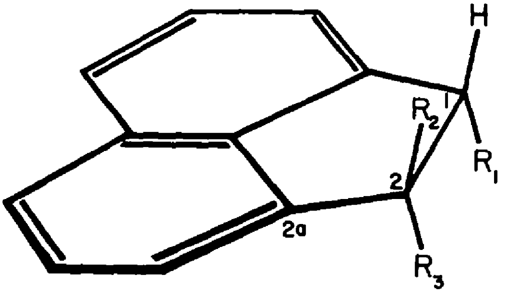
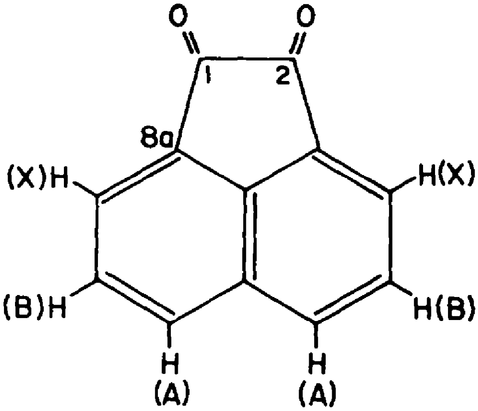
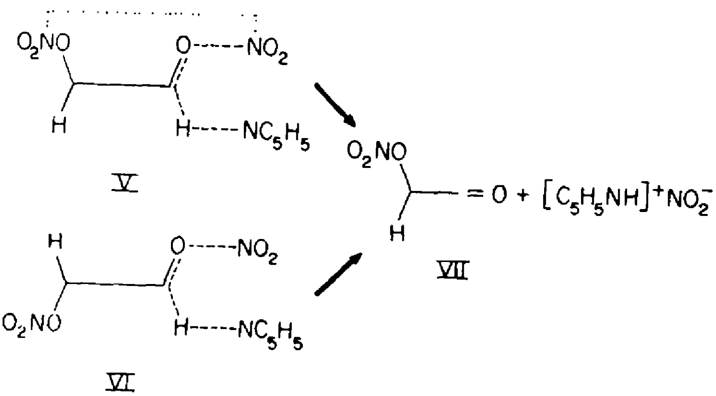


I R_1, R_2, R_3 = H
III R_1, R_3 = OH; R_2 = H
IV R_1, R_2 = OH; R_3 = H



II



purified by chromatography on a column of silica gel (Found: C, 82·4; H, 5·00. $C_{19}H_{14}O_2$ requires: C, 83·0; H, 5·13%). A similar separation applied to the oily product (434·0 mg) obtained from IV by this procedure yielded 5 fractions one of which was identified as *O*-benzylidene-*cis*-1,2-acenaphthenediol by its m.p. and PMR spectrum. The major fraction, although homogeneous, gave elemental analysis (Found: C, 72·3; H, 6·83%) and an IR spectrum which did not agree for IV or for an *O*-benzylidene derivative of III or IV.

Reaction of the dinitrates with pyridine. Dinitrate (2·76 mg) was washed into the solution bulb of a micro, all-glass, liquid–liquid extractor with anhydrous pyridine (0·100 ml) and the stoppered vessel was maintained at 25·0 ± 0·1°. After a measured time interval 2N H_2SO_4 (2 ml) was added and the solution was exhaustively extracted with ether. The residue from the ether extract was taken up in benzene (1·00 ml) and applied in 0·01 or 0·10 ml aliquots to Whatman No. 1 paper sheets which were developed as descending chromatograms with benzene–acetic acid–water (8:2:1 v/v.) The amount of unreacted dinitrate was determined spectrophotometrically directly from the developed and dried chromatograms. The area of the nitrate ester spot was determined by tracing it under UV light onto paper of known area/weight ratio (120·2 cm^2/g) and the traced spot was cut out and weighed. A 12 × 50 mm portion of the center of the nitrate ester spot was cut from the chromatogram and placed in the 0·5 cm cell holder in the spectrophotometer and a blank strip of equal size cut from a parallel position on the chromatogram was placed in the reference beam. The paper strips were painted with paraffin oil and the spectra (Table I) were recorded from 200 to 350 mμ. From these data the intensity of the light absorbed by the total nitrate spot was calculated as $\varepsilon = (\varepsilon_{max} - \varepsilon_{350}) \times$ spot area/1·44. Calibration curves relating ε and moles of dinitrate were prepared from chromatograms loaded with known quantities of the isomeric dinitrates. The percentage coefficients of variation were ±7·9% for the *cis*- and ±6·5% for the *trans*-isomer.

RESULTS AND DISCUSSION

It has long been assumed that fusion of the cyclopentane ring into the angular position of the naphthalene nucleus would force the acenaphthene molecule (I) into an essentially planar, rigid conformation with bisectional bonds[23] on C_1 and C_2.[24] The most recent X-ray[25] and computational[26] structural analyses indicated a planar molecule with a normal aliphatic peri-bond (C_1—C_2 = 1·54 ± 0·02 Å) and with steric strain shared out among the fused rings so that $\angle C_1C_2C_{2a} = 105{\cdot}2°$ and $\angle H_1C_1C_2 = 113{\cdot}5°$.

Dewar and Fahey[27] found the coupling constants for H_1 and H_2 in the PMR spectra of *cis*- and *trans*-1-deutero-2-bromoacenaphthene to be 7·4 and 1·9 cps respectively. The corresponding dihedral angles ($\angle H_1C_1C_2/C_1C_2H_2$) calculated from the Karplus equation[28] would be $\phi_{cis} = 18°$ or 24° and $\phi_{trans} = 119°$ or 117° depending on which of two sets of values[29] was selected for the constant J_0 in the equation. In the absence of the distortion to be expected from bulky bromine dihedral angles in the parent hydrocarbon (I) should therefore be approximately $\phi_{cis} = 0°$ and $\phi_{trans} = 120°$ as previoulsy assumed for fully-eclipsed bisectional bonds.[23]

The IR spectrum of a dilute carbon disulfide solution of pure 1,2-acenaphthenedione (II) showed a strong, single carbonyl band at 1721 cm^{-1} and no band near 1770 cm^{-1} was present. An unidentified solid impurity removed by ether extraction from crude preparation of II showed the same carboxyl absorption as well as a strong band

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at 1770 cm^{-1} and it appeared, therefore, that the previously reported[30] band at 1771 cm^{-1} (solid) and 1780 cm^{-1} (solution) was probably due to a similar impurity rather than steric effects.[31] Comparison with the carbonyl stretching bands in the solution spectra of 9,10-phenanthraquinone (1683 cm^{-1})[30,37] and benzocyclobutenequinone (1815, 1783 cm^{-1})[38] clearly showed that a pronounced shift to higher frequencies occurred in this series of aryl cyclic 1,2-diketones as the size of the ring was decreased.

TABLE 1. M.P. AND ULTRAVIOLET SPECTRA OF ACENAPHTHENE DERIVATIVES

Compound	M.p. (°C) Observed	M.p. (°C) Reported	Ultraviolet Spectra[a] λ_{max}(mμ)	Ultraviolet Spectra[a] log ε
Acenaphthene (I)[b]	96·0–96·5	96[32]	289·2[c]	3·813[c]
Acenaphthenequinone (II)	273–274	262[34]	302·6	3·764
			313·3	3·775
			338·0	3·404
1,2-Acenaphthenediol Derivatives				
cis-diol (III)	218·0–219·5	212[35]	285·3	3·778
trans-diol (IV)	160·0–163·0	159·5[35]	286·3	3·792
cis-diacetate	134·5–136·5	130[36]	284·7	3·877
trans-diacetate	Liquid[d]		285·1	3·895
cis-dibenzoate	148·0–149·5		285·3	3·938
trans-dibenzoate	132·0–134·0		285·3	4·032
cis-dinitrate[e]	128·0–130·5		285·3	3·878
trans-dinitrate[f]	98·5–99·5		286·5	3·902
cis-*O*-isopropropylidene	76–78	75·6–76·2[30]		
cis-*O*-benzylidene	126–129			
cis-carbonate	231·0			

[a] In 95% ethanol at 10^{-4} M.

[b] M.p. of picrate 165·5–166·0°; Lit. 162°.[32]

[c] Lit. λ 289·0 mμ, log ε 3·81[33]; six other maxima agreed within 1·0 mμ and log ε ± 0·04.

[d] B.p. 108°/0·02 mm.

[e] Found: N, 9·93%.
[f] Found: N, 10·17%
} Calc. for $C_{12}H_8N_2O_6$: N, 10·15%.

From X-ray analysis of our sample of II, Mak and Trotter[39] found the carbonyl oxygen to be approximately coplanar with and equidistant from both β-carbons ($O_1—C_2 = O_1—C_{8a} = 2{\cdot}41$ Å) and the $C_1—C_{8a}$ bond to have a mean length of 1·48 ± 0·01 Å. The $C_1—C_2$ bond length (1·53 ± 0·02 Å) was nearly identical to that in acenaphthene. It could be assumed that in solution also the carbonyl groups in the three cyclic diones would be more constrained to coplanarity as the size of the ring was decreased and the increase in carbonyl stretching frequency which accompanied ring

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contraction was therefore ascribed to enhancement of a similar type of steric interaction between the chromophores as has been described for other 1,2-diketones and α-haloketones.[24,31,40]

The structural symmetry of II in solution was confirmed by the PMR spectrum (in trifluoracetic acid) which showed the expected ABX multiplet for the aromatic protons and analysis[41] as shown in Table 2. The assignments (formula II) were readily apparent from the magnitudes of the *ortho*[42] amd *meta* coupling constants and the known deshielding effect of carbonyl groups.[41]

The UV spectrum of II (Table 1) showed vibrational splitting of the acenaphthene, $\pi \rightarrow \pi^*$ band which was shifted toward the red. This fact and the color change from light yellow to deep orange in the series 9,10-phenanthraquinone, acenaphthenequinone, benzocyclobutenequinone also suggested steric interaction of the vicinal carbonyl groups.

Assuming C—O bond length of 1·42 Å and fully eclipsed conformations, the inter-oxygen distances (R) were calculated as 2·67 Å and 3·50 Å for the *cis*- and *trans*-1,2-acenaphthenediols (III and IV) respectively. The former value was in good agreement with that (R = 2·71 Å) found by Mak and Trotter[39] in the crystal of III. These conformations were also consistent with the IR spectra of III and IV in dilute carbon tetrachloride solution.[43] The strength of the intramolecular, intra-oxygen hydrogen bonding in III ($\Delta\nu_s = 77\ \text{cm}^{-1}$) exceeded that in *cis*-1,2-cyclopentanediol ($\Delta\nu_s = 61\ \text{cm}^{-1}$) and in *cis*-1,2-cyclohexanediol ($\Delta\nu_s = 39\ \text{cm}^{-1}$)[43] for which the values of R were calculated as 2·70 Å and 2·74 Å respectively from the corresponding values of ϕ_{cis} of 46° and 50°.[44] On this basis it appeared that conformational rigidity played a more important role in the relative degree of hydrogen bonding than the equilibrium inter-oxygen distances. As would be expected from the larger R in IV, no intraoxygen hydrogen bond was found in the solution spectrum of the *trans*-diol[43] and this result was confirmed in the present work from the PMR spectrum on 0·5 M deuteroacetone solution which showed that H_1 and H_2 were coupled with their respective hydroxyl protons to give an AB quartet (J = 6·0 cps). The signal at lower field (τ 4·60) was assigned to H_1 and H_2 (Table 2) since the quartet collapsed to a single two-proton peak at this field strength on the addition of two drops of pyridine. The *cis*-diol (III) was only very slightly soluble in acetone and the PMR spectrum in acetic acid solution showed a single peak for H_1 and H_2 at τ 4·45 (Table 2).

Lead tetraacetate oxidation[45] also indicated only a minor degree of conformational flexibility in III and IV as compared to other cyclic 1,2-diols. The ratio k_{cis}/k_{trans} at 20° was 10^3 to 10^7 times larger for III and IV than for the 1,2-cyclopentanediols, the 1,2-cyclohexanediols and the 9,10-dihydro-9,10-phenanthrenediols. The fact that III was oxidized 3 to 24,000 times faster than the other *cis*-diols was probably due

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to similarity in conformation of the cyclic transition state and the initial state of III;[46] for the more flexible *cis*-diols the larger values of ϕ_{cis} in the initial states implied larger activation energies for the rate-determining step. Rate enhancement for III due to a "stretched" peri-bond[43] seemed less plausible in the light of the structural data presented above.

Although it has been stated or implied in the literature that *trans* vicinal hydroxyl groups in cyclohexane rings do not form cyclic ketals[47–49] the synthesis of the cyclic *O*-isopropylidene derivative of *trans*-1,2-cyclohexanediol[21] which was independently confirmed[50] constituted an exception to this "rule".[44] On the other hand Franz[50] showed that the internal carbonates of *trans*-1,2-cyclohexanediol and *trans*-1,2-cyclopentanediol were not formed under conditions which gave good yields of the cyclic esters of the corresponding *cis*-diols. In the present work cyclic carbonate, *O*-isopropylidene, and *O*-benzylidene derivatives were readily prepared from III and were characterized through their m.p, analyses, and spectra (Tables 1 and 2) and, for the carbonate, by hydrolysis to the parent diol. In contrast IV either did not react in the cyclization experiments or was converted to III or a derivative of III under forcing conditions. Other unidentified products obtained from IV in the acidic media probably resulted from a pinacol-pinacolone type of rearrangement.[51] It was

TABLE 2. PROTON MAGNETIC RESONANCE SPECTRA OF ACENAPHTHENE DERIVATIVES

Compound[a]	$\tau(H_1H_2)$	X $\tau(H_3H_8)$	B $\tau(H_4H_7)$	A $\tau(H_5H_6)$	|JBX| $J(H_3H_4)$	|JAB| $J(H_4H_5)$	|JAX| $J(H_3H_5)$
Acenaphthene	6·71						
Acenaphthenequinone[b]		1·61	2·11	1·80	7·4	7·4	1·4
1,2-Acenaphthenediol Derivatives							
cis-diol[c]	4·45						
trans-diol[d]	4·60[e]						
cis-diacetate[f]	3·87	2·62	2·89	2·87	6·5	6·6	<0·5
trans-diacetate[g]	3·99	2·63	2·91	2·90	5·9	6·5	<0·5
cis-dibenzoate	3·50						
trans-dibenzoate	3·54						
cis-dinitrate	3·27	2·54	2·82	2·74	8·8	6·6	1·0
trans-dinitrate	3·46	2·61	2·90	2·82	9·0	6·7	0·8
cis-*O*-isopropylidene[h]	4·57	2·69	2·97	2·88	5·5	6·5	5·5
cis-*O*-benzylidene	4·46						
cis-carbonate	3·92						

[a] In $(CH_3)_2$ CO except as noted below.
[b] In CF_3COOH
[c] In CH_3COOH
[d] In $(CD_3)_2$ CO
[e] After addition of two drops of pyridine.
[f] Acetoxy protons at τ 7·85($CHCl_3$).
[g] Acetoxy protons at τ 7·85($CHCl_3$).
[h] Isopropyl methyl protons: Me_1 τ 8·84, Me_2 τ 8·45 ($CHCl_3$).

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of interest in this connection that all attempts to synthesize acenaphthylene epoxide have so far been unsuccessful,[51,52] The above results, therefore, confirmed the presence of a high degree of conformational rigidity in the diols.

Direct nitration of III and IV in nitric acid-acetic anhydride-acetic acid involved competition of *O*- and *C*-nitration[53,54] and the pure dinitrate esters were separated from nuclear-substituted isomers by chromatography. The diol configurations were retained in the nitrates since catalytic hydrogenation[19] regenerated the corresponding parent compounds. The nitroxy group bands in the IR spectra of the dinitrates and of ethyl and benzyl nitrates fell within the frequency ranges previously assigned for polynitrates (Table 3) except as noted below. The multiplicity of Band I in the solid state spectra of the dinitrates was a function of the crystal structure as suggested by Guthrie and Spedding[55] rather than of intramolecular functional group interactions since the solution spectra showed a single, sharp band only in this region.

The published solution spectra of diethylene glycol dinitrate tetramethylolcyclopentanone tetranitrate, and tetramethylolcyclohexanol pentanitrate, also showed only single bands at this frequency.[58] On the other hand Simecek[10] considered the shift of this band from 1660 cm^{-1} in solid pentaerythritol mono- and tetranitrates to 1630–1645 cm^{-1} in undiluted liquid pentaerythritol di- and trinitrates to reflect intramolecular hydrogen bonding of nitroxy groups in the latter compounds. The band splitting of similar magnitude which occurred in the solid dinitrates of III and IV in the absence of hydroxyl groups suggested that Simecek's results might also be attributed to intermolecular interactions.

The significantly higher frequencies (9 and 16 cm^{-1}) of bands I and II in the solution spectrum of *cis*-1,2-acenaphthenediol dinitrate in cyclohexane compared to those of the same bands in spectra of *trans* isomer and the mononitrates (Table 3) indicated larger force constants for the antisymmetric and symmetric vibrations of the NO$_2$ group in the *cis*-dinitrate. On the basis of the interpretation already given for the spectra of the cyclic diketones, these shifts were taken as evidence of steric interactions of the contiguous nitroxy groups in the *cis*-dinitrate.[59] A similar elevation of the symmetric and antisymmetric N—O stretching frequencies in *o*-halogenonitrobenzenes relative to those in the *m*- and *p*-isomers and nitrobenzene has been reported.[60] The identification of Bands IV and V in the *cis*-dinitrate, shown in parentheses in Table 3, was tentative since the assignments were made to bands which appeared at frequencies closest to the specified ranges; the frequency of Band III, on the other hand, did not differ significantly among the four nitrate esters.

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[52] E. H. Charlesworth, H. Campbell, J. J. Conn, C. T. Elston and D. L. Stachiw, *Canad. J. Chem.* **35**, 351 (1957).

[53] E. D. Hughes, *Nitration, Papers Presented to the Kekule Symposium.* Butterworths, London (1959).

[54] E. L. Blackall, E. D. Hughes, C. K. Ingold and R. B. Pearson, *J. Chem. Soc.* 4366 (1958).

[55] R. D. Guthrie and H. Spedding, *J. Chem. Soc.* 953 (1960).

[56] D. M. W. Anderson, G. O. Aspinall, J. L. Duncan and J. F. Smith, *Spectrochim. Acta* **17**, 1001 (1961).

[57] R. A. E. Carrington, *Spectrochim. Acta* **16**, 1279 (1960).

[58] F. Pristera, M. Halik, A. Castelli and W. Fredericks, *Analyt. Chem.* **32**, 495 (1960).

[59] While this paper was in preparation a publication appeared by T. Urbanski and M. Witanowski, *Trans. Faraday Soc.* **59**, 1046 (1963) in which the same conclusion was reached based upon condensed-state spectra of a series of substituted di- and polynitrate esters.

[60] T. Kinugasa, *Nippon Kagaku Zasshi* **82**, 1473 (1961).

The UV spectra of the dinitrates, diols and diacetates were quite similar (Table 1) although the position and intensity of fine structure was characteristic for each type of substituent. In each case the maximum absorption of the *cis*-isomer was shifted by 0·4 to 1·2 mμ to shorter wavelengths whereas the isomeric dibenzoates gave nearly identical spectra. In the esters the $n \rightarrow \pi^*$ transitions of the nitroxy and carbonyl groups could not be distinguished from the large absorption due to the aromatic nucleus. The chemical shifts (τ values) of H_1 and H_2 in the esters and diols (Table 2) were inversely proportional to the apparent electronegativity of the *O*-substituent[61,62] and the signal from the *cis*-isomer appeared consistently at lower field than that of the *trans*-derivative. The aromatic protons in the diacetate, dinitrate, and *cis*-*O*-isopropylidene derivatives appeared in the spectra as an ABX multiplet analogous to that in the acenaphthenedione spectrum and the peaks were assigned in similar fashion as shown in Table 2. The aromatic multiplets in the spectra of acenaphthene, the diols, and the cyclic carbonate although clearly of the same type were insufficiently resolved for detailed analysis and, in the spectra of the benzoates and *O*-benzylidene derivatives, were superimposed on the signals from the phenyl protons. With

TABLE 3. INFRARED FREQUENCIES OF NITROXY GROUPS

Band	I	II	III	IV	V
Range (cm^{-1})[a]	1667–1613	1285–1267	871–833	759–738	716–685
Assignment	ν_a (NO_2)	ν_s (NO_2)	ν(ON)	γ_w (NO_2)	δ(NO_2)
Solution Spectra[b]					
Ethyl nitrate	1635	1279	846	756	696
Benzyl nitrate	1637	1276	842	750	694
trans-1,2-Acenaphthenediol dinitrate	1646	1276	843	750	705
cis-1,2-Acenaphthenediol	1655	1285	844	(779)[c]	(726)[c]
Condensed State Spectra					
Ethyl nitrate (neat)[d]	1625	1279	858	757	700
Benzyl nitrate (neat)[e]	1626	1278	860	756	697
trans-1,2-Acenaphthenediol dinitrate (KBr)	1649 1621	1283	860	754	708
cis-1,2-Acenaphthenediol dinitrate (KBr)	1648 1627	1294[f] 1278 1269	868	758	(728)[c]

[a] Assigned from condensed state spectra.[55–57]
[b] In cyclohexane, 10^{-2}M.
[c] Nearest band.
[d] The PMR spectrum showed no unassigned peaks.
[e] Prepared and purified according to Buncel and Bourns.[66]
[f] Strongest component.

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[61] B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.* **77**, 3977 (1955).
[62] P. R. Hammond, *J. Chem. Soc.* 2565 (1963).

the exception of the dibenzoates the UV and PMR spectra of the isomeric acenaphthene derivatives showed consistent small shifts between the *cis*- and *trans*-isomers with the greatest differences appearing in the spectra of the dinitrate esters. The cause of these shifts, which appeared to be real, remains obscure but they undoubtedly reflect different degrees of steric interaction of the vicinal groups with each other and with the aromatic nucleus.

The ^{14}N nuclear resonance spectra of the isomeric 1,2-acenaphthenediol dinitrates, benzyl nitrate, ethyl nitrate, *trans*-1,2-cyclohexanediol dinitrate and *meso*-hydrobenzoin dinitrate[63] in acetone solutions were recorded for us at 4 Mc by Dr. R. C. Jones of Varian Associates, Palo Alto, California, to whom we are most grateful. No significant differences were found in the chemical shifts of the nitrate nitrogen which were $\delta + 38 \pm 2$ ppm for the *cis*-acenaphthene derivative and $\delta + 39 \pm 2$ ppm for the *trans*-dinitrate measured from the nitrate ion signal as reference. A notable and unexplained difference among the spectra was the broadening by a factor of about five at half peak height in the signals from the aryl nitrates as compared with those from the aliphatic compounds.

From their X-ray analysis of the crystalline dinitrate of III, Mak and Trotter[39] found the two nitroxy groups to be planar and inclined to the plane of the acenaphthene skeleton at angles of 62·1° and 71·2°. The bond lengths and angles within the secondary nitroxy groups were:

$$\text{C—O} = 1{\cdot}46_8\ \text{Å},\ \text{O—NO}_2 = 1{\cdot}40_9\ \text{Å},\ \text{CON—O}' = 1{\cdot}20\ \text{Å},\ \angle\text{CON} = 115{\cdot}5^\circ,$$
$$\angle\text{ONO}' = 111^\circ \text{ and } 117^\circ \text{ and } \angle\text{O}'\text{NO}' = 132^\circ.$$

The closest approach of two nitroxy groups was 2·91 Å and occurred intramolecularly between the oxygen of one nitro group and the neighbouring alkoxyl oxygen; all other inter-group distances were greater than 3·0 Å. This distance of closest approach was greater than the sum of the van der Waals' radii of the oxygens (2·8 Å) and indicated the absence of conventional bonding between the *cis* nitroxy groups. On the other hand it seemed possible that in solvents of low dielectric constant the increased vibrational freedom would permit even closer approach of the relatively positive alkoxyl oxygen to the relatively negative oxygen atom of the nitro group. From examination of molecular models it appeared unlikely that the corresponding oxygen atoms in the *trans* isomer could approach within 3·0 Å without causing displacement of carbon atoms from the molecular plane.

The dinitrates were completely decomposed in boiling anhydrous pyridine in 30 minutes without evolution of nitrogen oxides. An unidentified nitrate ester intermediate which fluoresced under UV light was formed from both isomers at an early stage in the reaction and was rapidly transformed into acenaphthenequinone (II) and other products as the reaction proceeded. The quinone itself was only partially destroyed after boiling for 25 hours in pyridine solution. The dinitrates were also partially decomposed by pyridine in 25 hours at $-20°$ and nitrite ion was detected in the reaction mixture.[64] At $25{\cdot}0 \pm 0{\cdot}1°$ the decomposition rate was first-order to at least 70% conversion and the ratio k_{trans}/k_{cis} was 6·5.

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[63] I. G. Csizmadia and L. D. Hayward, to be published.

[64] P. Carboni, *Chemica e Industria, Milan* **36**, 825 (1954).

The formation of II as a major product indicated a carbonyl-forming elimination reaction similar to that observed with 9-fluorenyl nitrate and pyridine[65] and with alkoxide ion and benzyl nitrate.[66] The latter reaction was studied in detail by Buncel and Bourns[66] who showed that it occurred *via* a concerted mechanism in which the O—NO_2 bond was ruptured in the rate-determining step. The acenaphthenediol dinitrates contained both of the structural features known to favor this mechanism: (i) acidic α-hydrogen, and (ii), substituent groups capable of conjugation with the forming carbonyl group. The bimolecular character of the present reaction, however, was not apparent since pyridine functioned as both base and solvent. The absence of the above constitutional factors in the hexitol and dianhydrohexitol nitrates favored the alternative mechanism of nucleophilic attack by pyridine on the nitrate nitrogen.[7]

The transition states for the acenaphthenediol dinitrate reaction with pyridine could be formulated as shown in partial structures V and VI which represent C_1 and C_2 and their attached groups viewed along the molecular axis of symmetry with the dotted line to suggest interaction of the nitroxy groups in the *cis*-isomer (V). The 2-nitroxyacenaphthenone (partial structure VII) would correspond to the common intermediate detected, but not identified, among the primary reaction products from both dinitrates. The statistical probability of the pyridine attack at the α-hydrogens would appear to favor the formation of VI over that of V by a factor no larger than 2. The actual ratio of the apparent first-order rate constants (6·5) suggested that formation of V required expenditure of more energy than formation of VI due to the steric interaction of the nitroxy groups despite the fact that the α-hydrogens in V showed a τ value characteristic of more acidic protons.

Acknowledgments—We are grateful to Mr. T. C. W. Mak and Dr. J. Trotter for making available to us important new information in advance of publication and for their continued interest in the problem. One of us (I. G. C.) wishes to thank the National Research Council of Canada for a Studentship.

We also gratefully acknowledge the financial support of the Defence Research Board of Canada.

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[65] G. W. H. Cheeseman, *J. Chem. Soc.* 448 (1959).

[66] E. Buncel and A. N. Bourns, *Canad. J. Chem.* **38**, 2457 (1960).