1,8-Di-*tert*-butylnaphthalenes. Photochemistry and Mass Spectroscopy

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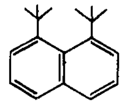
Peri di-*tert*-butylnaphthalenes have been photolyzed to afford hemi-Dewar isomers. Kinetic parameters for the thermal isomerization of the latter class of compounds have been obtained. Mass spectral data, including appearance and ionization potentials, have been obtained for the peri-crowded naphthalenes as well as their unstrained isomers.

In order to examine the conflict between steric bulk and aromatic character that is built into the 1,8-di-*tert*-butylnaphthalene system **1**, a series of photochemical and mass spectral experiments were undertaken in our laboratories.[1] The precedents for this work were developed in similar studies with the *o*-di-*tert*-butylbenzene system **2**.[2]



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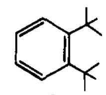

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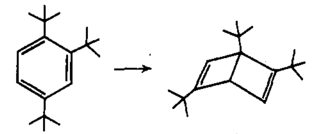
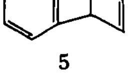
The seminal experiment in photochemistry and also in the field of aromatic valence isomers was that of van Tamelen and Pappas[2b] who converted 1,2,4-tri-*tert*-butylbenzene (**3**) to its Dewar isomer **4** by irradiation with Vycor-filtered uv light. Subsequent to that discovery, a systematic photochemical and synthetic research effort has succeeded in preparing and/or interconverting Dewar benzene, prismane, and benzalene isomers.



3 4

In the naphthalene field, the preparation of valence isomers has been largely a synthetic endeavor, and has to date afforded hemi-Dewar naphthalenes **5** and **6** and naphthvalene **7**.[3] There has been a long history of naphthalene photochemistry none of which has afforded valence isomers.[4] The most crowded naphthalene photolyzed heretofore was octamethylnaphthalene (**8**) which reacted with oxygen to form adduct **9** but exhibited no trace of valence isomer.[5]



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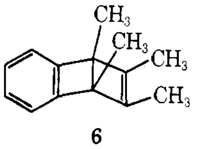

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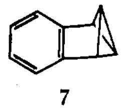

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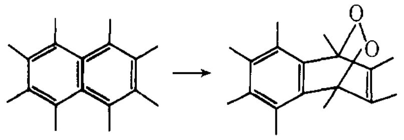

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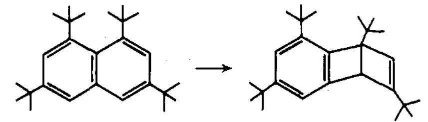
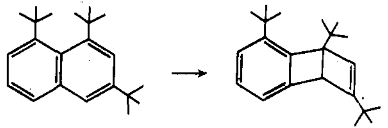
In our laboratory, the experiments were performed with the tetra-*tert*-butylnaphthalene **10**.[6] Irradiation in either cyclohexane or hexane using a Hanovia 450 W medium pressure lamp with Pyrex filter afforded a photoisomer **11** in 95% yield with a 5% remainder of **10**. This mixture is a photostationary state since **11**, purified by chromatography and recrystallization, afforded the same 95:5 composition upon irradiation.



10 11

The structure proof of **11** is based on its nmr (*tert*-butyls at δ 1.00, 1.13, 1.30, and 1.40; benzylic H at 3.91, vinyl H at 6.10, 2 aromatic H's at 6.89 and 7.08) which compares well with that of **5**. Further, thermal isomerization (*vide infra*) of **11** afforded **10** allowing us to discount any more deep-seated rearrangement. Our study continued with tri-*tert*-butylnaphthalene **12** which afforded isomer **13** under our standard conditions.



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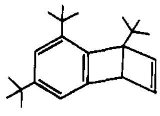
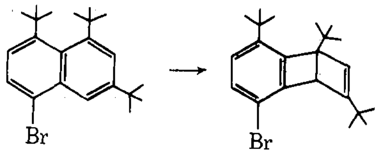


14

That the more heavily substituted ring was the one that isomerized was discerned from the nmr spectrum which had one less aromatic *tert*-butyl and one more aromatic hydrogen than that of **11**. Within the limits of analysis, we were unable to detect isomer **14**. We have no satisfactory explanation of this selectivity.

The multiplicity of the rearrangement of **10** was examined with the triplet quenchers piperylene and ferrocene (E_t 59 and 43 kcal/mol). No effect on the isomerization process was detected.[7] The bromo-*tert*-butyl derivative **15** was studied[8] with the presumption that the "heavy atom" effect[9] might allow triplet formation and perhaps some difference in photochemistry. However, the valence isomer **16** was the sole product obtained, with no evidence for **17** or any other valence isomer discernable.



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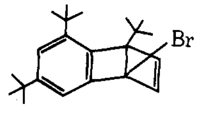

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The thermal reversal of the Dewar isomers was studied in some detail.[10] The rate constants for the rearomatization

Table I
Rate Constants, Half-Lives, and Activation Parameters for the Thermal Reversion of 11

Temp, °C	Rate constant, sec^{-1}	$t_{1/2}$, hr
38[a]		70
50	$1.07 \pm 0.19 \times 10^{-5}$	18.3
65	$5.8 \pm 0.8 \times 10^{-5}$	3.4
70[a]		2
80	$2.6 \pm 0.4 \times 10^{-4}$	0.75
E_a	24.0 ± 3.8 kcal/mol	
Log A	11.3 ± 2.4	

[a] Half-lives at these temperatures were computed for easy comparison to data for other valence isomers.

Table II
AP and IP Data for *tert*-Butylnaphthalenes (eV)

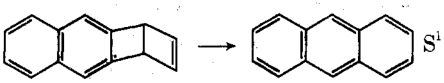
Isomer	AP	IP	Δ
12	7.14	9.58	2.44
24	7.76	10.36	2.60
25	7.68	10.30	2.62

Table III
Mass Spectra (70 eV) of *tert*-Butylnaphthalenes

Peak	Probable assignment	Rel intensity	Peak	Probable assignment	Rel intensity
1,4			1,3,8		
240	M^+	76	296	M^+	100
225	$M - CH_3$	100	281	$M - CH_3$	36
183	M − *t*-Bu	14	240	M − isobutylene	8
169		10	239	M − *t*-Bu	38
167		10	238	M − isobutane	5
165		10	237		7
			226		10
1,3			225		49
240	M^+	75			
225	$M - CH_3$	100	1,3,5,8		
183	M − *t*-Bu	5	352	M^+	100
169		5	337	$M - CH_3$	44
167		6	297		16
165		8	296	M − isobutylene	66
			295	M − *t*-Bu	9
1,3,6			294	M − isobutane	12
296	M^+	100	281		75
281	$M - CH_3$	82			
239	M − *t*-Bu	2	1,3,6,8		
			352	M^+	100
1,3,5			337	$M - CH_3$	19
296	M^+	100	297		6
281	$M - CH_3$	55	296		25
239	M − *t*-Bu	2.5	295		2
			294		5
			281		25

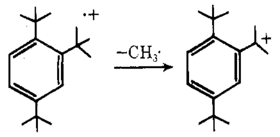
of **11** were determined using nmr integration. The results are presented in Table I. Comparable half-lives were observed for isomers **13** and **16**. These indicate a higher barrier to aromatization than that for the less substituted analog **5** ($t_{1/2}$ 4 hr, 38°) and a similar barrier to that of **6** ($t_{1/2}$ 1.5 hr, 70°). One factor in the higher energy can be assigned to the effects of *tert*-butyl rotation. In the aromatic compound **10**, the barrier to free rotation is 6 kcal/mol,[6a] determined at an nmr coalescence temperature of −137°. The comparable hindrance to rotation in the Dewar isomer **11** cannot be determined at the lowest temperature of operation of the spectrometer, therefore presumably less than that of **10**.[11]

The adiabatic isomerization of electronically excited valence isomers to electronically excited states of parent aromatics has been observed recently. Naphthvalene **7** upon flash photolysis affords triplet naphthalene,[12] while anthracene valence isomer **18** affords singlet anthracene **19** upon excitation.[13] Similar experiments performed by Professor Turro's group at Columbia with **11** and **16** did not yield observable aromatic excited states, presumably because these states have a dark pathway, namely valence isomerization, available for energy consumption.

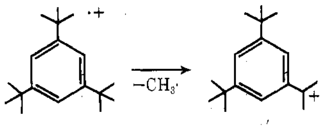


18 **19**

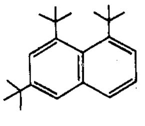
From the excited states of photochemistry we turn to those of mass spectroscopy to obtain one datum desired in the 1,8-di-*tert*-butylnaphthalene series: the calorimetric strain energy as a comparison to that of the *o*-dibutylbenzenes. We chose a mass-spectroscopy method developed by Arnett.[14] He compared the increment in energy between the appearance potential of the molecular ion and the ionization potential for the M − 15 peak. When the increments in unstrained di-*tert*-butylbenzenes were compared to the increments of *o*-di-*tert*-butylbenzenes, it was noted that the strained cases required ~1 eV less energy which in kcal/mol compares quite favorably to the strain energy determined by calorimetry. The assumption implicit in these experiments was that a crowded *tert*-butyl group in 1,2,4-tri-*tert*-butylbenzene (**20**) loses a methyl group to form a dimethylbenzyl cation **21** which is not significantly more crowded than the cation **23** derived from 1,3,5-tri-*tert*-butylbenzene (**22**). Thus, any difference in energy for the loss of CH_3 was assigned to a difference in ground-state energy of the isomers, namely strain energy in the more crowded **20**. This assumption hsn been analyzed more rigorously by Jalonen and Pihlaja.[15] With this precedent to encourage us, and with the 1000-fold greater quantities required for conventional combustion calorimetry to discourage us, we determined appearance potentials (AP) of the molecular ions of naphthalenes **12**, **24**, and **25** and ionization potentials (IP) of their M − 15 fragments. The method of semilog plots of ion abundance *vs.* electron energy with krypton and acetone as calibration standards was used.[16] The results are presented in Table II.



20 **21**



22 **23**



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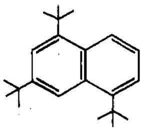

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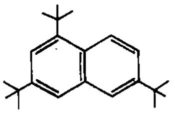

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It can be seen that the increments between AP and IP of crowded and uncrowded *tert*-butylnaphthalenes are essentially equal. Thus, the extrapolation of Arnett's technique to our series breaks down. The rationale for this nonextrapolation is simply that the nonhindered *tert*-butyl is participating in the loss of $CH_3\cdot$ presumably because there is insufficient relief of strain energy in the loss of methyl from a crowded *tert*-butyl group. Further, our analysis of nmr data has postulated a great deal of nonplanarity in the peri-crowded region so that the *tert*-butyls are not true "aromatic" *tert*-butyls. Thus, their interaction with radical cation of the molecular ion would not be the same as "aromatic *tert*-butyls" and they would not be forming a true planar dimethylbenzyl cation as the methyl radical was departing. This presumed lack of "reactivity" of peri *tert*-butyls finds an interesting parallel in the acid-catalyzed reactions discussed in our earlier work.

The routine 70 eV mass spectra in the series produced no unusual observations (Table III). We searched carefully for evidence of bis elimination of methyl and hydrogen or two methyls to form a less-strained ring, but no such peaks were observed. This may be contrasted to data obtained for 4,5-dimethylphenanthrene by Dougherty, *et al.*[17]

Experimental Section

Photochemistry. General Procedure. The naphthalene to be photolyzed was placed in an 8 in. long reaction vessel (capacity *ca.* 150 ml) with a 50/60 ground glass female joint and dissolved in 120 ml of spectral grade solvent. A water-cooled immersion well with a 50/60 ground glass male joint (lightly greased with Nonaq stopcock grease) containing a Pyrex filter and a 450 W, type L Hanovia high-pressure mercury lamp, catalog No. L6′, was inserted into the reaction vessel and the magnetically stirred solution subjected to photolysis. The progress of the photolysis was followed by removing a sample of the photolysate and subjecting it to uv analysis (PE-202, hexane), monitoring the disappearance (usually about 48 hr) of the maximum at *ca.* 310 nm, which is characteristic of 1,8-di-*tert*-butylnaphthalenes. The uv sample was then returned to the reaction vessel. After the photolysis was judged complete, the solvent was evaporated under reduced pressure at *room temperature* and the residue was dissolved in pentane and filtered through 1 g of activity II neutral alumina contained in a Pasteur pipet using pentane as the eluent. The pentane was evaporated at *room temperature* and the residue was used without further manipulation for the kinetic runs or other experiments.

2,4,8,10-Tetra-*tert*-butyltricyclo[4.4.0.0^{2,5}]deca-3,6,8,10-tetraene, (5,6-Benzo-1,3,7,9-tetra-*tert*-butylbicyclo[2.2.0]hexa-2,5-diene or 1,3,7,9-Tetra-*tert*-butyl Hemi-Dewar Naphthalene) (11). A sample of 0.128 g (0.363 mmol) of 1,3,6,8-tetra-*tert*-butylnaphthalene was photolyzed for 48 hr. At the end of this time the hexane was evaporated and the yellow-white solid filtered through activity II neutral alumina using pentane as the eluent. The pentane was evaporated to yield 0.128 g (100%) of a white solid shown by nmr (CCl_4) to consist of 95% photoproduct **11** and 5% starting material. The above solid (0.028 g) was recrystallized from a minimum amount of warm (45°) methanol to yield 0.009 g (32%, first crop only, the yield was not maximized) of pure (by uv) photoproduct: mp 57–58°; ir (CCl_4) 3.45, 6.87, 6.93, 7.29, 7.42, 9.19, and 11.51 μ; nmr (CCl_4) δ 1.00 (9 H, s, C_1-*tert*-butyl), 1.13 (9 H, s, C_3-*tert*-butyl), 1.30 (9 H, s, C_7-*tert*-butyl), 1.38 (9 H, s, C_9-*tert*-butyl), 3.91 (1 H, d, J = 1.5 Hz, methine H), 6.10 (1 H, d, J = 1.5 Hz, vinyl H), 6.89 (1 H, d, J = 1.5 Hz, H_7 or H_9), and 7.08 ppm (1 H, d, J = 1.5 Hz, H_9 or H_7); uv max (hexane) 273 (2.83) and 282 nm (log ϵ 2.82).

Anal. Calcd for $C_{26}H_{40}$: C, 88.57; H, 11.43. Found: C, 88.44; H, 11.41.

The same results were obtained using spectral grade cyclohexane as the solvent, or at 5° using hexane as the solvent.

2,4,10-Tri-*tert*-butyltricyclo[4.4.0.0^{2,5}]deca-3,6,8-10-tetraene (5,6-Benzo-1,3,9-tri-*tert*-butylbicylo[2.2.0]hexa-2,5-diene or 1,3,9-Tri-*tert*-butyl Hemi-Dewar Naphthalene) (13). A sample of 0.062 g (0.209 mmol) of 1,3,8-tri-*tert*-butylnaphthalene was photolyzed for 48 hr. At the end of this time, the hexane was evaporated and the yellow oil filtered through activity II neutral alumina using pentane as the eluent. The pentane was evaporated to yield 0.062 g (100%) of a colorless oil shown by nmr (CCl_4) to consist of 90% photoproduct **13** and 10% starting material. Attempts to either induce crystallization or separate the valence bond isomer by chromatography were a failure. The tri-*tert*-butyl hemi-Dewar naphthalene had the following spectral characteristics: nmr (CCl_4) δ 1.00 (9 H, s, C_1-*tert*-butyl), 1.13 (9 H, s, C_3-*tert*-butyl), 1.38 (9 H, s, C_9-*tert*-butyl), 3.97 (1 H, d, J = 1.5 Hz, methine H), 6.14 (1 H, d, J = 1.5 Hz, vinyl H), and 6.67–7.17 ppm (3 H, m aromatic H); uv max (hexane, 10% naphthalene impurity subtracted out) 272 (2.67) and 279 nm (log ϵ 2.60).

7-Bromo-2,4,10-tri-*tert*-butyltricyclo[4.4.0.0^{3,5}]deca-3,6,8,10-tetraene (16). A photolysis of 0.055 g (0.2 mmol) of 5-bromo-1,3,8-tri-*tert*-butylnaphthalene was carried out under nitrogen. After 15 hr the material was passed through a gram of activity grade II alumina with hexane elution and yielded 0.050 g (91%) of an isomer: ir (CCl_4) 1100, 1130, 1365, 1385, 1450, 1465, 1550, 2900 cm^{-1}; nmr (CCl_4) δ 7.08 (1 H, d, Ha of AB quartet, J_{AB} = 8.5 Hz), 7.04 (1 H, d, Hb of AB quartet, J_{AB} = 8.5 Hz); 6.15 (1 H, d, J = 1.5 Hz), 3.95 (1 H, d, J = 1.5 Hz), 1.40 (9 H, s), 1.18 (9 H, s), 1.09 (9 H, s).

Anal. Calcd for $C_{22}H_{31}Br$: C, 70.57; H, 8.35; Br, 21.34. Found C, 70.59; H, 8.48; Br, 21.21.

Kinetics of the Thermal Reversion of the Hemi-Dewar Naphthalenes to Naphthalenes. A sample (0.033–0.50 g) of the hemi-Dewar compound was dissolved in 0.35 ml of spectral grade CCl_4 and filtered into an nmr tube. The tightly stoppered nmr tube was then placed into a preheated oil bath at the temperature the reversion was being studied (50, 65, or 80°). The temperature of the oil bath was maintained by a Therm-O-watch temperature controller (I^2R, Model No.L-621, T = ±0.6°). At various times (about every 4–6 hr at 50°, every hr at 65°, and every 10–15 min at 80°) the nmr tube was removed from the oil bath and as quickly as possible placed into ice water for 2 min. The nmr tube was wiped free from water and as quickly as possible an nmr spectrum of the appropriate region was taken. The ratio of hemi-Dewar naphthalene and naphthalene at various times was determined by integration of the appropriate nmr signals. For the tetra-*tert*-butyl compound, the nmr spectral absorptions corresponding to the signals of the aromatic protons of the hemi-Dewar compound (δ 6.89 and 7.08) and the signals of the aromatic protons in the naphthalene (δ 7.22 and 7.48) were integrated and the ratio of areas was obtained after correcting for the number of protons. For the tri-*tert*-butyl compound, the nmr spectral absorptions corresponding to the olefin signal (6.14 δ) of the hemi-Dewar compound and the signals of the *entire* aromatic region (δ 6.67–7.6) were integrated and the ratio of areas was obtained after correcting for the number of protons. From these ratios, first-order plots were obtained (7–10 data points per run), the best straight line being determined by least-squares analysis (using a Compucorp 025 Educator calculator, program No.8802464). The rate constants and half-lives were then calculated from the slope of the straight line. Two runs were done at each of the three temperatures and the value of the rate constant (and half-life) at a particular temperature was taken as the average value of the two runs at that temperature. The average value of the rate constant at a particular temperature was then used for the energy of activation calculation. The three data points thus obtained were subjected to least-squares analysis (above) to find the equation of the best straight line from whose slope and intercept E_a and the value of log A were respectively determined.

Acknowledgment. We are indebted to Professor G. Epling of this department and Professor N. Turro of Columbia University for extensive discussions of our photochemical experiments. R.W.F. is most grateful to Lord Todd and Dr. Dudley Williams of Cambridge University for making available laboratory facilities in order to carry out the mass spectroscopy. Further, gratitude is owed to Dr. Adrian Yeo for the AP and IP measurements at Cambridge and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—**10,** 22495-86-9; **11,** 40155-12-2; **12,** 22495-89-2; **13,** 40155-13-3; **15,** 53535-11-8; **16,** 53535-12-9; **24,** 37754-74-8; **25,** 26157-41-5; 1,4-di-*tert*-butylnaphthalene, 10565-10-3; 1,3-di-*tert*-butylnaphthalene, 22495-85-8.

References and Notes

(1) (a) Taken in part from the Ph.D. dissertation of W.L.M., Fordham University, 1974. (b) Some of the photochemical results were the subject of a preliminary communication: W. L. Mandella and R. W. Franck, *J. Amer. Chem. Soc.*, **95**, 971 (1973).

(2) (a) For a review, see E. E. van Tamelen, *Accounts Chem. Res.*, **5**, 186 (1972); (b) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962).

(3) (a) R. N. McDonald, D. G. Frickey, and G. M. Muschik, *J. Org. Chem.*, **37**, 1304 (1972); (b) R. N. McDonald and D. G. Frickey, *J. Amer. Chem. Soc.*, **90**, 5315 (1968); (c) D. T. Carty, *Tetrahedron Lett.*, 4753 (1969); (d) T. J. Katz, E. J. Wang, and N. Acton, *Amer. Chem. Soc.*, **93**, 3782 (1971).

(4) For a review of naphthalene photochemistry, see ref 1a.

(5) H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4269 (1972); *J. Chem. Soc. D*, 254 (1972). The unstrained 1,3-di-*tert*-butylnaphthalene is a stable product of a novel photocycloreversion; J. H. Boyer and K. G. Srinivasan, *J. Chem Soc. D*, 699 (1973).

(6) Details of the preparation of the (a) tri-*tert*-butylnaphthalene (**12**) are reported in J. E. Andersen, R. W. Franck, and W. L. Mandella, *J. Amer. Chem. Soc.*, **94**, 4109 (1972); (b) tetra-*tert*-butylnaphthalene (**10**), R. W. Franck and E. G. Leser, *J. Org. Chem.*, **35**, 3932 (1970).

(7) In flash experiments kindly performed by Dr. Arthur Lyons in Professor N. Turro's laboratory, no phosphorescence of the triplet state of **10** could be detected. We thank Professor Turro for permitting the disclosure of his experiments.

(8) The preparation of **15** will be described in a separate article: K. J. Falci and R. W. Franck, manuscript in preparation.

(9) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodonleas, *J. Phys. Chem.*, **66**, 2499 (1962).

(10) (a) For a review of thermal isomerizations of aromatic valence isomers, see ref 1a. (b) For the observation of benzene triplets in thermal isomerization, see P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3025 (1973).

(11) J. E. Andersen, unpublished results. We thank Dr. Andersen for permitting the reporting of his experiments.

(12) N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnahan, and T. J. Katz, *J. Amer. Chem. Soc.*, **95**, 2035 (1973).

(13) N. C. Yang, R. V. Carr, E. Li, J. K. McVey, and S. A. Rice, *J. Amer. Chem. Soc.*, **96**, 2297 (1974).

(14) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5389 (1967).

(15) J. Jalomen and K. Pihlaja, *Org. Mass Spectrom.*, **6**, 1293 (1972).

(16) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 14.

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(18) Commercially available chemicals were used as supplied except where noted. Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Boiling points are uncorrected. Analyses were determined by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were recorded on Perkin-Elmer Model 137 and 337 spectrophotometers. Ultraviolet spectra were taken on a Cary 15 spectrophotometer. Nmr spectra were recorded on Varian A-60A and XL-100 instruments with signals reported relative to internal tetramethylsilane. The multiplicity of signals is reported as follows: singlet, s; doublet, d; triplet, t; quartet, q; multiplet, m; broad, br; envelope, ev; and exchange with deuterium oxide, ex. Analytical and preparative thin-layer chromatography was done using silica gel GF-254 and alumina GF-254, Type E, purchased from the Brinkmann Instruments Co. Florisil (60–100 mesh) was obtained from the Fisher Scientific Co. Silica gel and alumina for dry column chromtography, which was done according to the method of Loev and Goodman, *Chem. Ind.* (*London*), 2026 (1967), was bought from Waters Associates. Neutral alumina, activity II, was purchased from Woelm.

Infrared Liquid-Phase Chemiluminescence from Reactions of Bis(2,4,6-trichlorophenyl) Oxalate, Hydrogen Peroxide, and Infrared Fluorescent Compounds

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Several polycyclic aromatic hydrocarbon derivatives provide infrared fluorescence quantum yields on the order of 0.30 in solution. The infrared fluorescers were combined with a peroxyoxalate chemiluminescent system based on bis(2,4,6-trichlorophenyl) oxalate to provide solution-phase infrared chemiluminescence with quantum yields as high as 0.06 einstein mol^{-1}. The effect of fluorescer concentration on chemiluminescence quantum yield indicated the theoretical maximum yield of excited emitter to be 49% with the fluorescer 16,17-dihexyloxyviolanthrone. Theoretical considerations relating to infrared fluorescence and chemiluminescence are discussed.

Infrared chemiluminescence, unlike visible chemiluminescence, is unlikely to be discovered by accidental observation, and few examples are known. The examples are confined to gas-phase reactions which produce vibrationally excited states,[1] to emission from singlet oxygen,[2] and to reaction of violanthrone with singlet oxygen.[3]

It is well recognized that efficient liquid-phase chemiluminescence requires the efficient formation of an electronically excited singlet product in a chemical reaction and that the excited product must be an efficient fluorescer.[4,5] The modification of a chemiluminescent reaction to produce emission in a specified spectral region is generally difficult, however. Most chemiluminescent reactions produce their excited products directly from the energy releasing reactants, and it is difficult to modify the structure of the fluorescent product while at the same time retaining the efficient excitation capability of the reactant.[6]

Peroxyoxalate chemiluminescence, however, differs from most chemiluminescent reactions in that the emission spectrum depends on the fluorescence spectrum of a compound which is added independently of the reactants.[7,8] Through the use of a variety of fluorescers, emission almost spanning the visible spectrum has been obtained.[7–9] This property, along with its inherent efficiency, encouraged us to select the peroxyoxalate reaction as the basis for infrared chemiluminescence research.

The peroxyoxalate reaction of bis(2,4,6-trichlorophenyl) oxalate with hydrogen peroxide and sodium salicylate was chosen because this reaction has been shown to provide quantum yields as high as 0.20 einstein mol^{-1} with the fluorescer rubrene.[10] A search of the literature for organic infrared fluorescers failed to reveal an acceptable prospect, although several dyes have been reported to luminesce in the infrared on fibers,[11] and several red fluorescers have spectral distributions extending into the infrared in solution.[12] Two useful criteria are available for fluorescer design. First, the intrinsic probability of radiative transition from an excited electronic level increases with the extinction coefficient of the electronic absorption of that level.[13] Thus, compounds having extinction coefficients above about 10^4 have a relatively high fluorescence probability. Secondly, according to Stokes' law the emission spectral distribution of an organic fluorescer in general approximates the mirror image of the absorption spectrum and