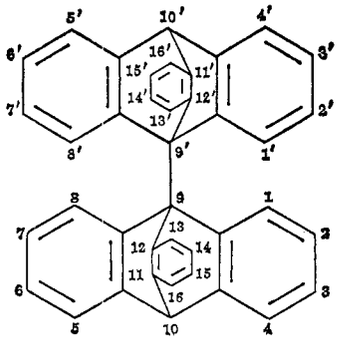

I

further, to confirm the structure assignment made by Bartlett and Greene for their "compound x." The present synthesis of bitriptycyl involves the addition of benzyne to 9,9′-bianthryl. For this purpose, benzyne was generated from anthranilic acid,[6] 1,2-bromofluorobenzene,[7] and 1,2,3-benzothiadiazole 1,1-dioxide.[8] The yields of bitriptycyl ranged from approximately 5–20%. The synthesis involving benzyne generated from anthranilic acid was the most convenient and generally gave the highest yields and the purest product. The isolation of bitriptycyl was considerably simplified by the extreme insolubility of this hydrocarbon in acetone. Bitriptycyl melts at 577° with decomposition, and in the absence of oxygen appears to be thermally stable up to its melting point.

The proof of structure of bitryptycyl is based on the following facts. Carbon and hydrogen analysis is consistent with the formula $C_{40}H_{26}$. The mass spectrum shows a base peak at *m/e* 506 (molecular ion), a strong peak at *m/e* 253 (triptycyl ion plus a double charged molecular ion) and a metastable ion at approximately *m/e* 127. These data serve to establish the molecular weight and also indicate that cleavage of the molecular ion to the triptycyl ion is an important process. The ultraviolet spectrum, $\lambda_{max}^{dioxane}$ 280 mμ (log ε 3.69), 272 (3.63), and 266 (sh) (3.38), compares favorably with the ultraviolet spectrum of triptycene, $\lambda_{max}^{dioxane}$ 279 mμ (log ε 3.67), 271 (3.55), and 265 (sh) (3.32). The infrared spectrum is relatively simple and agrees with the published spectrum of Bartlett and Greene's "compound x."

Our interest in the bitriptycyl system arises from the possibility that suitably substituted derivatives, *e.g.*, a 2,2′-disubstituted bitriptycyl, may exhibit conformational stability. We are presently investigating this possibility.

Experimental Section

Infrared and ultraviolet spectra were determined on Perkin-Elmer Model 137 and Cary Model 14 spectrophotometers, respectively. Mass spectra were determined on an Associated Electrical Industries MS-9 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. The melting point of bitriptycyl is uncorrected.[9]

Reaction of 9,9′-Bianthryl and Anthranilic Acid and *n*-Butyl Nitrite.—Solutions of anthranilic acid (4.12 g, 30 mmoles) and *n*-butyl nitrite (3.49 g, 34 mmoles), each in 27 ml of 2-butanone, were simultaneously added during a 3.5-hr period to a stirred refluxing solution of 9,9′-bianthryl[10] (0.50 g, 1.4 mmoles) in 25 ml of 2-butanone. The *n*-butyl nitrite solution was always in slight excess over the anthranilic acid solution. The reaction mixture was refluxed for an additional 1 hr and allowed to stand at room temperature for at least 12 hr in order to ensure complete precipitation of the product. The solid was filtered and repeatedly triturated with acetone. Two crystallizations from nitrobenzene gave a white solid: mp 577 ± 5° dec; ν^{Nujol} 1284 (w), 1151 (m), 1133 (w), 1036 (m), 915 (m), 808 (m), 771 (m), 753 (m), 745 (s), and 738 (s) cm^{-1}; $\lambda_{max}^{dioxane}$ (10-cm cell) 280 mμ (log ε 3.69), 272 (3.63), and 266 (sh) (3.38); *m/e* 506 (base peak), *m/e* 253 (56% of base peak), and *m/e* approximately 127 (metastable ion). For comparison, triptycene has $\lambda_{max}^{dioxane}$ 279 mμ (log ε 3.67), 271 (3.55), and 265 (sh) (3.32).

Anal. Calcd for $C_{40}H_{26}$: C, 94.83; H, 5.17. Found: C, 94.96; H, 5.15.

Acknowledgment.—The authors thank Dr. William Milne of the National Institutes of Health for the measurement and interpretation of the mass spectra.

(6) L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).
(7) G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).
(8) G. Wittig and R. W. Hoffmann, *ibid.*, **95**, 2718 (1962).
(9) The melting point of bitriptycyl was determined in a sealed tube, under nitrogen, using a zinc chloride bath and a 100–620° partial-immersion thermometer, supplied by the Chemical Rubber Company, Cleveland, Ohio.
(10) F. Bell and D. H. Waring, *J. Chem. Soc.*, 1579 (1949).

Magnetic Nonequivalence of a Thiophosphate Ester

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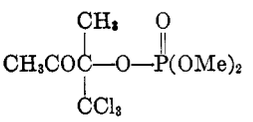
Magnetic nonequivalence due to molecular asymmetry has been reported for a variety of compounds.[1-3] Roberts, *et al.*,[4] studied nmr spectra of 1-phenylethyl benzyl ether and related compounds. In particular, the effect of the proximity of an asymmetric center on the extent of magnetic nonequivalence was investigated. Sidall and Prohaska[5] have observed nonequivalence of the alkoxyl groups on a variety of phosphorus esters. This effect was explained by a preferred conformation of these esters. Bentrude[6a] recently reported that



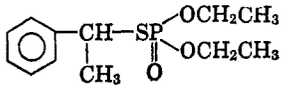
shows magnetically nonequivalent methoxyl groups (Δ = 4 cps), ascribed to the asymmetric carbon in the molecule.

(1) E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963).
(2) J. K. Randall, J. J. McLeskey, III, P. Smith, and M. E. Hobbs, *ibid.*, **86**, 3229 (1964).
(3) R. M. Moriarty, *J. Org. Chem.*, **30**, 600 (1965).
(4) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964).
(5) T. H. Siddall and C. A. Prohaska, *ibid.*, **84**, 3467 (1962).
(6) (a) W. G. Bentrude, *ibid.*, **87**, 4026 (1965). (b) It was pointed out by a referee that the nonequivalence in this compound presumably originates in a folded conformation I of higher energy than some open conformation II, and increasing the temperature increases the population of I.

I II

TABLE I

SOLVENT EFFECT ON THE NONEQUIVALENCE[a]



Solvent	Dipole moment	Dielectric const	Chemical shift of methyl triplet $-P(OCH_2CH_3)_2$		Separation of triplets, cps
Neat			1.17		0
Nonpolar					
Carbon tetrachloride	0	2.3	1.17	1.26	5
Hexachlorobutadiene	0	2.57	1.13	1.22	5
Benzene-d_6	0	2.28	0.93	0.98	3
Carbon disulfide	0	2.64	1.13	1.21	4
Polar					
Chloroform-d	1.02	4.80	1.23	1.24	1
Acetonitrile	3.84	30	1.20	1.21	1
Acetone	2.89	20.7	1.20		0
Dimethyl sulfoxide	3.9	45	1.18	1.19	1
Pyridine	2.22	5.8	1.18		0

[a] All the spectra (except the first) were run with ~10 vol % of the compound in the above solvents at ambient temperature. Chemical shift values are in parts per million downfield from tetramethylsilane (internal standard).

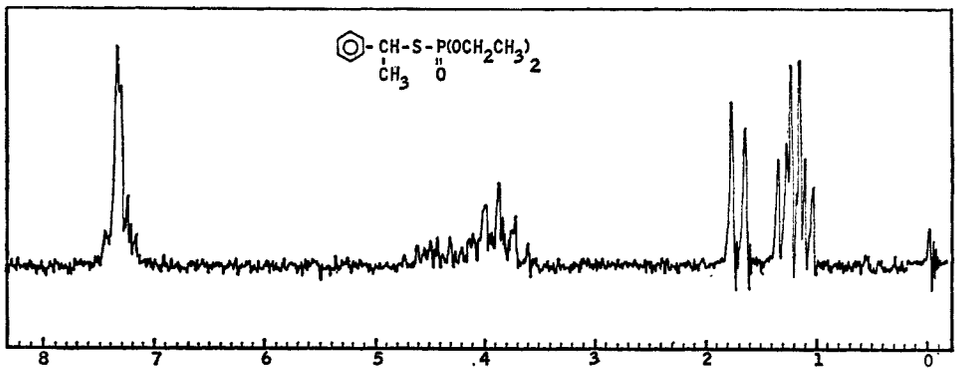


Figure 1.

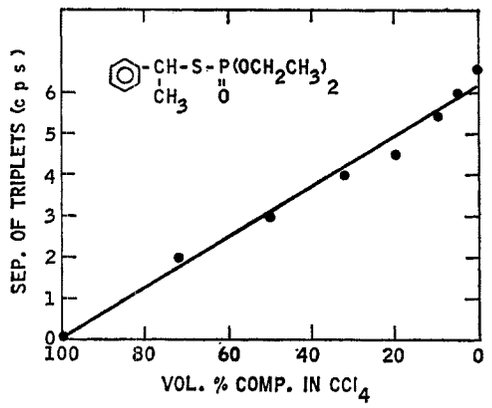
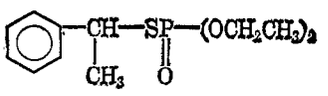


Figure 2.—Effect of concentration on nonequivalence.

We now wish to report magnetical nonequivalence of protons separated from an asymmetric carbon center by a distance of six bonds. This effect was observed in O,O′-diethyl S-(α-phenylethyl)thiophosphate, I (Figure 1).[7] The nmr spectrum of I in CCl_4 shows two triplets



I

(7) The spectra were taken on 20% solutions in CCl_4. They were recorded with a Varian Associates A-60 high-resolution spectrometer. Chemical shifts are in parts per million downfield from tetramethylsilane.

(Δ = 5 cps) for the methyls of the ethoxy groups. The separation of these triplets is too large to be a long-range splitting caused by coupling with the phosphorus nucleus (spin 0.5). It must be the result of the two methyls being magnetically nonequivalent. The long-range coupling with the phosphorus nucleus was observed on an expanded scale and found to be J_{POC-CH_3} = 0.6 cps. The separation of the triplets in CCl_4 depends on the compound's concentration as shown in Figure 2. The greatest separation of the two triplets (Δ = 6.5 cps) was observed at 1 vol % concentration. When the compound was run without solvent at ambient temperature only one triplet was observed. At 100°, however, two triplets (Δ = 2 cps) appeared.[6b] An 80 vol % solution in CCl_4 was observed at different temperatures in order to establish that the chemical shift of the two methyl groups had not crossed over in going from a dilute solution at ambient temperature to a neat solution at 100°. The separation of the triplets was 1.4 cps at 30° and 2.2 cps at 75° for the 80% solution. The fact that the separation increased with increasing temperature indicates that the triplets of the methyl groups had not crossed over. The values in Figure 2 are measured at ambient temperature.

We have also studied the effect of other solvents on the nonequivalence of these ethoxy groups. The separation of the triplets was greatest (~5 cps) in nonpolar solvents and became 0 (0–1 cps) in polar solvents. The results are listed in Table I and the

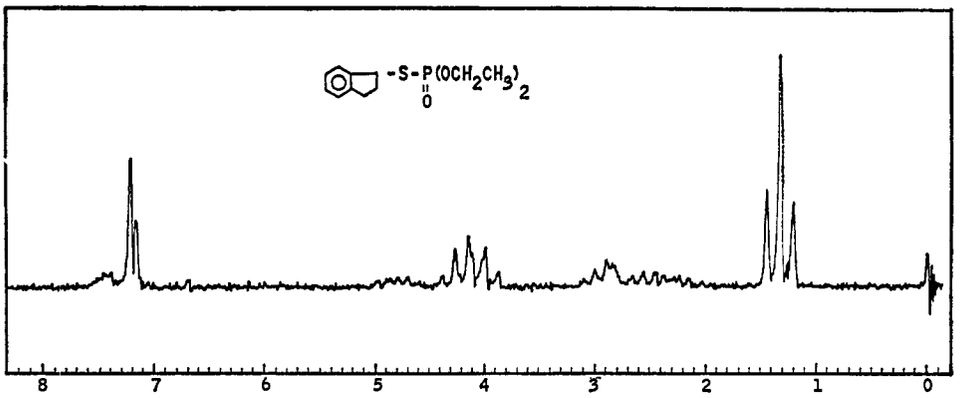


Figure 3.

last column shows clearly the difference between the effect of polar and nonpolar solvents.

These results are in qualitative agreement with the finding of Roberts and co-workers.[8] They reported that in the case of 1-phenylethyl benzyl ether the degree of magnetic nonequivalence bears an approximate inverse relation to the dielectric constant of the solvent.

In view of the preceding, it was surprising to find that O,O′-diethyl S-(1-indanyl)thiophosphate did not show a similar nonequivalence for the ethoxy groups (Figure 3). It should be noted in this connection that Roberts[8] also found, that, in contrast to the methylene group in 1-phenylethyl benzyl ether, the corresponding protons in indanyl benzyl ether were equivalent in all solvents investigated.

We have also studied a number of similar thiophosphates not containing an aromatic ring moiety and they all exhibit a single triplet at 1.33 ppm for all the methyl protons of the ethoxy groups. The indanylthiophosphate (Figure 3) also shows a triplet at this position demonstrating that the π system of the benzene ring does not effect the methyl's chemical shift. In contrast, the two triplets from compound I are both shifted upfield. Thus, the two ethoxy groups apparently experience diamagnetic shielding, although to a different extent.

More data will be necessary in order to draw valid conclusions as to the possible factors causing this nonequivalence. We feel, however, that the data supplied here are of interest to workers in this field and may stimulate such further research.

(8) G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1058 (1965).

2-Amino-4,6-diazido-1,3,5-triazine

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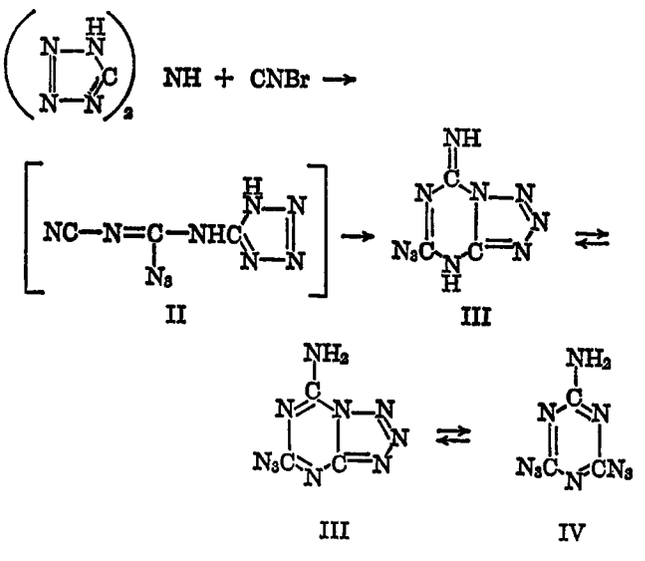
The opening of the ring in 5-(substituted-amino)-tetrazoles by cyanogen bromide to give substituted cyanoguanyl azides was recently examined in some detail.[1] When an attempt was made to extend this to the preparation of 2,4-diazido-1,5-dicyano-1,3,5-triaza-1,4-pentadiene (I), NC—N=C(N_3)NHC(N_3)=NCN, from the disodium salt of bis(5-tetrazolyl)amine and 2 molar equiv of cyanogen bromide, there was obtained a base-insoluble product whose infrared spectrum revealed azido function at 2140 cm^{-1} (Nujol mull or N,N-dimethylformamide solution), but unexpectedly no nitrile function (cyanoguanyl azides show both functions). In addition the compound remained unchanged when treated with base under conditions which convert cyanoguanyl azide derivatives to tetrazolines.[1] A better yield of the same compound was realized when only 1 mole of cyanogen bromide was employed per mole of bis(tetrazolyl)amine.

The analytical data indicated that only one cyano group, rather than two, had been introduced per mole of starting bis(tetrazolyl)amine. Reduction of the compound with hydrogen sulfide in ammoniacal aqueous ethanol gave sulfur and melamine. A structure consistent with all of these facts is 2-amino-4,6-diazido-1,3,5-triazine (IV), whose formation can be depicted by Scheme I. One of the tetrazole rings is opened by the

SCHEME I



cyanogen bromide in the expected fashion to yield II which then undergoes an intramolecular cyclization

(1) W. P. Norris and R. A. Henry, *J. Org. Chem.*, **29**, 650 (1946).