(7) into the thiazole skeleton 8 on treatment with phenacylidene–triphenylphosphorane (Scheme IV) was found in the literature.[10] The novel ring reorganization reported in this paper may be viewed as an intramolecular version of the above intermolecular reaction.

Experimental Section

Melting points were uncorrected. IR spectra were recorded on a JASCO A-100 spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian XL-100 spectrometer. ^{13}C NMR spectra were taken on JEOL FX-90Q spectrometer. All chemical shifts are reported in δ units downfield from Me_4Si, and the J values are given in hertz. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra were obtained with a JEOL JMS-01SG-2 spectrometer at 75 eV. UV spectra were measured on a Hitachi 340 recording spectrophotometer. All reactions were carried out under a nitrogen atmosphere.

3-Thioxo-5-phenyl-(*E*)-*N*-styrylisothiazole (3). To a solution of 3-oxo-5-phenyl-(*E*)-*N*–styrylisothiazole (2) (84.5 mg, 0.303 mmol) in pyridine (1.3 mL) was added phosphorus pentasulfide (76.6 mg, 0.345 mmol) by portions. The mixture was stirred for 3 h at room temperature. After addition of water the mixture was extracted with CH_2Cl_2, and the extracts were washed with 2 N HCl and saturated aqueous $NaHCO_3$ and then dried over Na_2SO_4. Removal of the solvent gave 70 mg (78% yield) of crude **3** as orange crystals, which, without purification, was subjected to the following reaction: ^{1}H NMR δ 6.08 (s, 1 H), 6.08 (d, 1 H J = 14.3 Hz), 7.0–7.7 (m, 10 H), 7.92 (d, 1 H, J = 14.3 Hz); IR ($CHCl_3$) 1178 cm^{-1}; MS, m/z (relative intensity) 295 (M^+, 16%).

(*Z*)-2-[2-(Methylthio)-2-phenylethenyl]-5-phenylthiazole (5). To a solution of **3** (56.5 mg, 0.19 mmol) in 2 mL of dichloromethane was added 28.3 mg (0.19 mmol) of freshly prepared trimethyloxonium tetrafluoroborate. The resulting mixture was stirred at room temperature for 2 h. To the stirred solution was added aqueous K_2CO_3 solution. The mixture was extracted with dichloromethane, and the combined extracts were dried over Na_2SO_4. The solvent was removed, and the residue was chromatographed on silica gel (containing 5% water), eluting with chloroform to give **5** (36.3 mg, 61% yield) as orange crystals. Recrystallization from ether gave a sample: mp 59–60 °C; ^{1}H NMR δ 2.15 (s, 3 H), 7.20 (s, 1 H), 7.34–7.65 (m, 10 H), 8.02 (s, 1 H); IR (KBr) 1585, 1485, 1475, 1442, 1150, 780, 755 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ) 242 (4.05), 279 (3.91), 360 (4.43) nm; MS, m/z (relative intensity) 309 (M^+, 100), 294 (49), 276 (42), 262 (39), 134 (42). Anal. Calcd for $C_{18}H_{15}NS_2$: C, 69.78; H, 4.89; N, 4.53; S, 20.72. Found: C, 69.77; H, 4.91; N, 4.54; S, 20.55.

(*Z*)-2-[2-(Methylsulfonyl)-2-phenylethenyl]-5-phenylthiazole (6). A solution of MCPBA (80%, 109 mg, 0.51 mmol) in CH_2Cl_2 (2.6 mL) was added dropwise with stirring at 0 °C to a solution of **5** (78 mg, 0.25 mmol) in CH_2Cl_2 (3.4 mL). After further stirring at room temperature for 2.5 h, the solution was washed with 5% aqueous $NaHSO_3$ and saturated aqueous $NaHCO_3$ and then dried over Na_2SO_4. Removal of the solvent gave **6** quantitatively as pale yellow crystals: mp 164–165 °C (recrystallized from ethyl acetate); ^{1}H NMR δ 3.03 (s, 3 H), 7.27–7.62 (m, 10 H), 7.29 (s, 1 H), 8.05 (s, 1 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 42.96, 127.1, 128.8, 129.1, 129.3, 129.4, 129.6, 130.8, 133.6, 135.5, 139.6, 142.0, 145.2, 157.8; IR (KBr) 1605, 1295, 1130, 800 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ) 260 (3.69), 346 (4.37); MS (75 eV), m/z 341 (M^+, 18), 340 (39), 262 (100), 134 (40). Anal. Calcd for $C_{18}H_{15}NO_2S_2$: C, 63.32; H, 4.43; N, 4.10; S, 18.78. Found: C, 63.15; H, 4.32; N, 4.15; S, 18.52.

Single-Crystal X-ray Diffraction Analysis of (*Z*)-2-[2-(Methylsulfonyl)-2-phenylethenyl]-5-phenylthiazole (6). The crystal data for **6** (single crystal obtained via recrystallization from ethyl acetate) are as follows: $C_{18}H_{15}NO_2S_2$, M = 341.43, monoclinic, space group $P2_1/a$, a = 9.290 (2) Å, b = 22.938 (3) Å, c = 8.521 (1) Å, β = 117.39 (1)°, V = 1612.1 (4) Å^3, Z = 4, D_c = 1.41 g cm^{-3}. Intensity data were collected by a Syntex R3 diffractometer in the range of $2 < 2\theta < 55°$ by using the monochromated Mo Kα radiation (λ = 0.71069 Å). The intensities of the three standard reflections were monitored every 100 reflections, and no significant variation was observed throughout the date collection. The data were corrected for Lorentz and polarization effects. Of 3783 collected reflections, 2826 were considered observed at the level of ($|F_o| \geq 3\sigma|F_o|$). The structure was solved by the direct method (MULTAN78) and refined anisotropically by the full-matrix least-squares process. All the hydrogen atoms, located on a difference Fourier map, were included in the final part of the refinement with the isotropic temperature factors to give the final agreement indices R = 0.050 and R_w = 0.046. The weights were of the form $w = 1/\sigma^2 (F_o)$. The final difference electron density map was featureless with the largest residual peak of 0.26 e/Å^3.[11] All the calculations were carried out on a HITAC M-200H computer at Hiroshima University with the structure analysis program system UNICS3.[12]

Registry No. 2, 110567-91-4; **3**, 116503-11-8; **5**, 116503-12-9; **6**, 116503-13-0.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, interatomic distances, and interatomic angles for **6** (3 pages). Ordering information is given on any current masthead page.

---

(10) Chauhan, M. S., Hassan, M. E.; McKinnon, D. M. *Can. J. Chem.* **1974**, *52*, 1738.

(11) Tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **6** have been deposited as supplementary material.

(12) Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem. Res.* **1979**, *56*, 1.

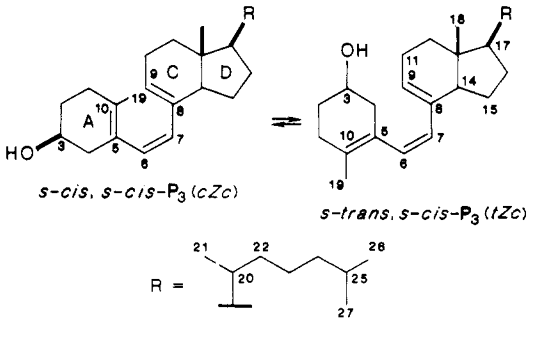
NMR Spectroscopic Investigation of Previtamin D_3: Total Assignment of Chemical Shifts and Conformational Studies

William G. Dauben* and Dirk J. H. Funhoff[1]

Department of Chemistry, University of California, Berkeley, California 94720

Received January 25, 1988

The two different classes of conformations of previtamin D_3 (P_3) are thought to lead upon irradiation to different products (ground-state conformational control,[2a] NEER principle[2b]). The two types of conformations proposed are shown in the following scheme. The thermal formation of vitamin D_3 occurs predominantly from one specific *cZc* conformation:[3]



---

(1) Recipient of a Feodor Lynen-Fellowship of the Alexander von Humboldt-Stiftung 1986–1988.

(2) (a) Dauben, W. G.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 4285. Dauben, W. G.; Phillips, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 5780. (b) Vroegop, P. J.; Lugtenburg, J.; Havinga, E. *Tetrahedron* **1973**, *29*, 1393. Jacobs, H. J. C.; Gielen, J. W. J.; Havinga, E. *Tetrahedron Lett.* **1981**, *22*, 4013.

(3) Berman, E.; Friedman, N.; Mazur, Y.; Sheves, M.; Zaretskii, Z. V. I. *Proc. Workshop Vitam. D, 4th* **1979**, 65. Sheves, M.; Berman, E.; Mazur, Y.; Zaretskii, Z. V. I. *J. Am. Chem. Soc.* **1979**, *101*, 1882.

0022-3263/88/1953-5376$01.50/0

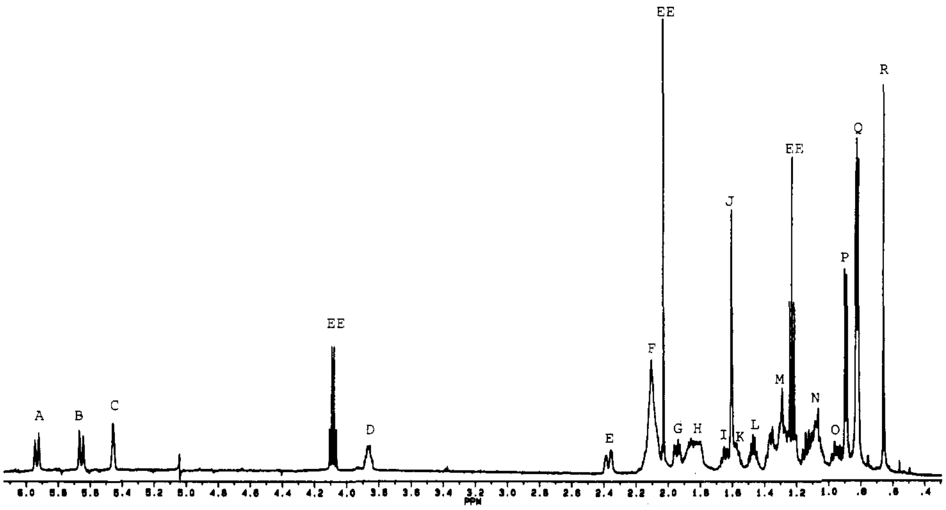


Figure 1. ^{1}H NMR spectrum of P_3 at −6.5 °C in $CDCl_3$. The letters refer to the assignment given in Table I; EE refer to signals of ethyl acetate, contained as an impurity in the sample.

Each of these types, represented planar in the above scheme, can be described as a mixture of two or more conformations, twisted around the triene moiety with different helicity. Consequently, a minimum total of four conformations could exist in solution. Recent molecular mechanics calculations[4] are in agreement with this postulation and have shown that the four minimum energy conformers, having enthalpies of formation within 3 kcal/mol with respect to the global minimum, are two *cZc* and two *tZc* forms.

In view of the important role these conformations play in the proposed explanations for the chemistry of P_3, it is surprising that no detailed conformational study can be found in the literature. The available information is mainly based on UV and CD data, which were interpreted as arising from only one group of conformations, *cZc* forms.[5] There is only one study reported in which, besides UV and CD measurements, a NOE experiment was used to determine the conformation.[5c] It was found, that irradiation of 9-H enhances a signal at 2.2 ppm. This signal was assigned to incorporate 4β-H besides 1β-H, 2α-H, and three other hydrogens, based on lanthanide-induced shifts (LIS). The two direct neighbors (11-H) were assigned to be at 1.85 ppm. It was concluded, that a *tZc* form is present, because this conformation allows 9-H and 4β-H to come close together. In fact, if the observed enhancement would be due to 4β-H, it would point to a specific helicity in the triene moiety, i.e., the A ring has to be above the plane of the C, D rings, hence a (+)*tZ*(−)*c* conformation[6] must be present. This specific conformation (with the OH group in the A ring being pseudoequatorial) was calculated to be the global energy minimum for P_3;[4] the published interpretation of the NOE spectrum is consequently in line with later theoretical considerations. Nevertheless, it is startling that in the experiment no enhancement due to the presence of *cZc* conformations was observed, which were calculated to be almost as abundant as *tZc* conformations and were proposed as the most stable forms by the cited investigator.[5c] In the above experiment a NOE enhancement of the 19-methyl group would then be expected.[7]

Table I. ^{1}H NMR and ^{13}C NMR Chemical Shift Assignments for P_3 in $CDCl_3$ at −6.5 °C (Letters Refer to the Group of Signals in the ^{1}H NMR Spectrum of P_3 (Figure 1))

atom no.	chemical shift ^{1}H	chemical shift ^{13}C	signal in ^{1}H NMR spectrum	mult
1	2.11	29.76	F	m
2	1.81 α	30.88	H	m
	1.58 β		K	m
3	3.85 α	67.46	D	m
4	2.37 α	37.36	E	d (J = 14.7 Hz)
	2.11 β		F	m
5		125.61		
6	5.93	128.49	A	d (J = 11.8 Hz)
7	5.66	128.82	B	d (J = 11.9 Hz)
8		136.42		
9	5.46	124.59	C	d (J = 3.5 Hz)
10		129.77		
11	2.11	24.81	F	m
12	1.36 α	39.90	M	m
	1.95 β		G	m
13		41.85		
14	2.11	50.63	F	m
15	1.64 α	23.33	I	m
	1.22 β		M	m
16	1.29 α	28.32	M	m
	1.86 β		H	m
17	1.13	54.15	N	m
18	0.66	11.14	R	s
19	1.61[9]	19.72	J	s
20	1.36	36.10	M	m
21	0.89	18.66	P	d (J = 6.5 Hz)
22	0.95 + 1.29	35.98	M + O	m + m
23	1.13 + 1.29	23.74	M + N	m + m
24	1.07	39.34	N	m
25	1.45	27.96	L	m
26, 27	0.82	22.52, 22.84	Q	2 d(J = 6.6 Hz)

The lack of such an observation and the ambiguity of LIS-based assignments prompted us to begin a more thorough investigation. A two-dimensional NOE experiment (NOESY) should be able to detect all possible dipolar hydrogen interactions, providing conformational information in greater detail, but its interpretation requires the complete knowledge of the ^{1}H NMR spectrum of P_3.

---

[4] Dauben, W. G.; Funhoff, D. J. H. *J. Org. Chem.*, in press.

[5] (a) Sanders, G. M.; Pot, J.; Havinga, E. *Prog. Chem. Org. Nat. Prod.* **1969**, *27*, 131. (b) Gielen, J. W. J. Thesis, University of Leiden, 1981. (c) Maessen, P. A. Thesis, University of Leiden, 1983.

[6] The sign indicates the sign of the torsional angle in question, following the rules of Klyne and Prelog (Klyne, W.; Prelog, V. *Experientia* **1960**, *12*, 521). "+" refers to clockwise deviation from 0° being s-cis, "−" to counter-clockwise rotation.

[7] The 19-CH_3 signal, although quite broad, shows no distinct coupling, even after applying resolution-enhancing methods on the acquired FID.

Presently, a complete assignment has not been reported.

Therefore, COSY, DEPT, and CH correlation measurements[8] were performed on a solution of P_3 in $CDCl_3$ which was cooled to −6.5 °C to slow down the vitamin D_3 formation.[9] Phase-sensitive NOESY spectra[10] were acquired to gain the conformational information needed; the assignment of the α- and β-hydrogens was also based on these spectra. the gathered data allowed an almost complete unequivocal assignment of the ^1H and ^{13}C spectra, with the exception of the 22- and 23-hydrogens in the side chain, which were assigned in accordance with the published assignment for vitamin D_3.[11] The full assignment of P_3 obtained in this study is given in Table I. The ^1H NMR spectrum is shown in Figure 1. The conformations of the A ring have been studied in detail.[4,5c] The OH group can adopt either a pseudoequatorial or -axial position, but both conformations allow *cZc* or *tZc* conformations regarding the triene moiety. According to the molecular mechanics calculations,[4] the same hydrogens of the A and C rings come close together in one given *tZc* or *cZc* conformation regardless of the two possible conformations of the A ring. It is therefore not important to know the exact conformation or the position of the equilibrium in the A-ring conformations.

The chemical shift of each hydrogen determined in this study is very like a mean value of the chemical shifts of this particular hydrogen in each of the different conformations that were interconverting rapidly. The conformational information is therefore lost in the ^1H NMR spectra; however, the NOESY spectrum will, as mentioned above, provide the desired information. During the relaxation time a hydrogen may interact with different neighbors in different conformations, consequently giving rise to a cross peak with all of them, provided that the rate of interconversion is fast compared to the relaxation time.

A representative NOESY spectrum is shown in Figure 2. The important cross peaks are labeled: 6-H ↔ 19-H and 9-H ↔ 19-H. These correlations clearly demonstrate the presence of both the *tZc* and the *cZc* conformations. The interaction between 6-H and 19-H is only possible in the *tZc* form and 9-H can only correlate with 19-H in the *cZc* form. Neither form can give both cross peaks; the distances between 9-H and the 19-H is too far in the *tZc* forms and, correspondingly, 6-H can not interact with 19-H in the *cZc* forms. This is true, regardless of the helicity of the triene moiety. Consequently, both conformations have to be present at the temperature of the measurements and, of course, at higher temperatures. In our calculations,[4] the $(+)tZ(-)c$ conformation was identified as the most stable one. In all of the *tZc* geometries, the closet distances between 6-H and 19-H were 1.9–2.0 Å. In the *cZc* conformations the distances between 9-H and 19-H were calculated to be in the range of 2.6–2.8 Å. Therefore, the second interaction should be of lower intensity, assuming comparable relaxation times. This can qualitatively be seen in the given spectrum (Figure 2).

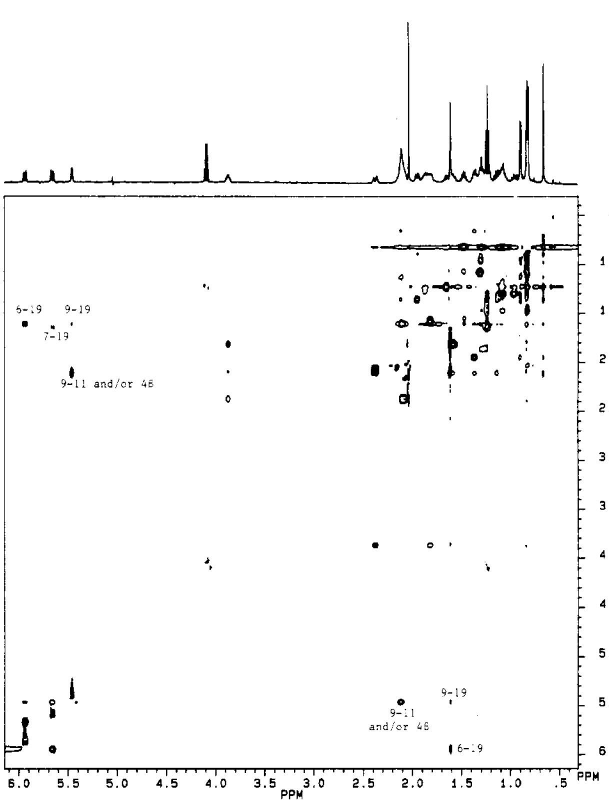


Figure 2. Phase-sensitive NOESY spectrum of P_3 at −6.5 °C in $CDCl_3$; mixing time 1.6 s, unsymmetrized. Shown are the negative levels only. The normal ^1H spectrum is plotted on the top. The numbers on some of the cross peaks refer to the carbon atoms directly bonded to the interacting hydrogens.

One would like to be able to gain information about the helicity of the triene moiety. It can be anticipated without closer examination that correlation of the two 4-H with 9-H or 6-H would depend on the exact geometry of the triene. All possible correlations between these hydrogens, not visible in the presented NOESY spectrum (Figure 2), can be observed at smaller mixing times. In the *cZc* forms, the cross peaks 4α-H ↔ 6-H and 4β-H ↔ 6-H are expected to be observable regardless of the helicity of the triene. The calculated distances are in the range 2.4–3.1 Å; hence one can not discriminate between the two *cZc* conformers. In the *tZc* conformations, the situation is more complicated. The distances between 4β-H and 9-H in the $(+)$-$tZ(-)c$ form are calculated to be 2.1 Å, regardless of the A-ring conformation. Consequently, a cross peak is expected and is actually observed. Unfortunately, the two 11-H resonate at the same position as 4β-H and they will, as direct neighbors of 9-H, certainly give a correlation peak. (This fact cast doubt upon the interpretation of the one-dimensional NOE experiment quoted.[5c] The observed enhancement may well be solely due the 11-hydrogens.) Therefore, it can not be determined, whether $(+)tZ(-)c$ is actually present or not. In the case of $(-)tZ(+)c$, 4α-H comes close to 9-H, about 2.1 Å. But the existence of the corresponding (weak) cross peak is not conclusive, because the distance 4α-H ↔ 9-H in the $(+)tZ(-)c$ with an equa-

---

[8] The spectra were recorded on a Bruker AM-500 (^1H: 500.135 MHz; ^{13}C: 125.759 MHz). Standard pulse sequences were used, i.e., DEPT.AU for the DEPT measurements, COSYPH.AU (Bodenhausen, G.; Kogler, H.; Ernst, R. R. *J. Magn. Reson.* **1984**, *58*, 370) for the phase-sensitive COSY spectrum, XHCORRD.AU (Bax, A. *J. Magn. Reson.* **1983**, *53*, 517. Rutar, V. *J. Magn. Reson.* **1984**, *58*, 306) for the normal CH correlation and a version of this optimized for a long-range CH couplings (Reynolds, W. F.; Enriquez, R. G.; Escobar, L. I.; Lozoya, X. *Can. J. Chem.* **1984**, *62*, 2421).

[9] For the preparation of P_3, see: Dauben, W. G.; Phillips, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 355. The P_3 was isolated and purified by MPLC using a Lobar-Lichroprep Si60 (40–63 μm) column, Merck 10401, and a 15/85 mixture of ethyl acetate/hexane.

[10] The P_3 sample was degassed with three freeze–pump–thaw cycles; the T_1 relaxation times were measured to be in the range of 0.5–1.6 s. One spectrum was recorded by using the Bruker pulse sequence NOESYPH.AU (Bodenhausen, G.; Kogler, H.; Ernst, R. R. *J. Magn. Reson.* **1984**, *58*, 370) with a mixing time of 1.6 s. Two other spectra were obtained simultaneously, with mixing times of 0.5 s and 1.2 s, using an in-house program, MOESY2PH.AU (Meyerhoff, D. J.; Nunlist, R.; O'Connell, J. F. *Magn. Reson. Chem.* **1987**, *25*, 843).

[11] (a) Wing, R. M.; Okamura, W. H.; Rego, A.; Pisio, M. R.; Norman, A. W. *J. Am. Chem. Soc.* **1975**, *97*, 4980. (b) Berman, E.; Luz, Z.; Mazur, Y.; Sheves, M. *J. Org. Chem.* **1977**, *42*, 3325. In the course of our study, the given assignments for vitamin D_3 could mainly be confirmed, the position of 14-H could be fixed at 1.96 ppm, but the assignment of the two 19-H have to be reversed, based on NOESY data.

torial OH group is only 3.0 Å, making a correlation possible. No information regarding the helicity of the triene can be obtained, based upon the interatomic distances derived from molecular mechanics calculations.[4]

Summary. The presented two-dimensional NOE experiments establish the first direct experimental evidence for the existence of two groups of conformations of P_3 in solution, i.e., *tZc* and *cZc*. This is in contrast to earlier interpretations based on UV and CD data[5] but is in agreement with molecular mechanics calculations.[4] Therefore, the chemistry of P_3 is determined by a complicated conformational equilibrium, which can be important with regard to the explanations for the observed wavelength effect in the photochemistry of P_3.[2]

Acknowledgment. This research was supported by Grant No. DK00709, National Institute of Diabetes and Digestive and Kidney Research. We express our appreciation to Molecular Design Ltd. for the generous donation of computer software and to J. Ralph of the U.C. Berkeley NMR facility for many discussions and helpful suggestions.

Registry No. Previtamin D_3, 1173-13-3.

Synthesis and Some Properties of 11,12-Diaminodibenzo[*b*,*g*][1,8]naphthyridine

S. Shi and F. Wudl*

Institute for Polymers and Organic Solids, Department of Physics, University of California, Santa Barbara, California 91036

Received March 4, 1988

In a recent series of papers a number of "proton sponges" have been studied with particular emphasis on their kinetic versus thermodynamic acidities.[1] In this paper we present the synthesis and pK_a determination of a novel heterocycle containing the elements of a "proton sponge". With this research, we wanted to ascertain the effect of electron-withdrawing functional groups (C═N) and steric crowding (two peri hydrogens) on the proton chelating moiety consisting of two 1,5 coplanar and rigidly disposed amino groups. Whereas we did not succeed in the preparation of a tetramethylated, exact equivalent to the 1,8-diaminonaphthalene archetype, we did prepare a desmethyl heterocycle, which is the subject of this report. We also report on the preparation of *p*-phenylenediaminobis(cyanoacrylonitrile) by a double barrel Curtius-type rearrangement.

Syntheses and Discussion

The title compound was prepared in an economical four-step sequence from readily available starting materials as shown in Scheme I. In the scheme, five steps are shown, but in fact steps c and d are carried out in a one-pot procedure without purification of the vinyl azide. The first two steps are based on work of Moore[2] but with improvement in yield. The Curtius-type rearrangement was published on a similar system[3] and in our hands proceeded efficiently, affording the aniline-trapped product in ~70% yield. Finally, the acid-catalyzed ring closure occurred smoothly at room temperature.

To test if our synthetic scheme was a general method to build up aza analogues of the acenes, we set out to prepare a tetraazaheptacene as shown in Scheme II.

The preparation of compound **3** was described by Moore and Robello[2] and, in our hands, the yields were found to vary over a wide range.[4]

We were able to show through the usual analytical techniques that molecule **5** had formed (even though mass spectroscopy was in perfect agreement with the proposed structure, elemental analysis results were slightly lower than calculated values for C and N, probably due to the hygroscopic nature of **5**), i.e., the Curtius rearrangement had taken place as expected. Unfortunately we have not been able to find conditions to afford the desired azaheptacene in isolable form. Changes in acid, solvent, and temperature did not yield material devoid of nitrile stretching mode absorption ($2190\ \mathrm{cm}^{-1}$) in the infrared. From this result we concluded that a polymer based on reaction of intermediate compound **4** with *p*-phenylenediamine was not going to be convertible to a polymer analogous to the Moore–Robello system.[5]

The title compound was isolated in the form of a yellow, microcrystalline powder containing one molecule of water. Double sublimation produced a yellow powder that still contained 0.4 molecules of water per formula unit, as determined by elemental analysis. The water of hydration is not detectable by mass spectroscopy. The compound is soluble in most polar organic solvents and THF (tetrahydrofuran) and essentially insoluble in nonpolar solvents. The pK_a was determined (spectrophotometrically)[6] to be 3.3 ± 0.2 in 80% (v/v) DMSO (dimethyl sulfoxide)/water. This compares with a pK_a value of 3.3 ± 0.2 for 9-aminoacridine (4.52 for 9-aminoacridine in water[7]), 2.2 ± 0.2 for 1,8-diaminonaphthalene (4.61 for 1,8-diaminonaphthalene in water[1]), and 12.34 for *N*,*N*,*N*′,*N*′-tetramethyl-1,8-diaminonaphthalene in water.[1] As can be seen, the title compound is actually a relatively weak base with a pK_a identical with that of 9-aminoacridine. This result could imply that the protonation site of the title compound and 9-aminoacridine is actually the heterocyclic nitrogen. It is possible that the tetramethyl derivative will be a stronger base.[8] So far all attempts to methylate [CH_3I, $(CH_3O)_2SO_2$] compound **1** have failed. Either no methylation was observed or, under more vigorous conditions, only noncharacterization reaction mixtures were obtained.

It has not escaped our notice that the structural features of the title compound could have important implications in regard to (a) internucleotide intercalation into

---

(1) (a) Alder, R. W.; Bowman, P. S.; Steele, W. R. S.; Winterman, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 723. (b) Alder, R. W.; Goode, N. C.; Miller, N. *J. Chem. Soc., Chem. Commun.* **1978**, 89. (c) Staab, H. A.; Saupe, T.; Krieger, C. *Angew. Chem. Int., Ed. Engl.* **1986**, *25*, 451. Staab, H. A.; Saupe, T.; Krieger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 731. (d) Zirnstein, M. A.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 460.

(2) Moore, J. A.; Robello, D. R. *Macromolecules* **1986**, *19*, 2667. (a) We thank Professor Moore for a copy of the relevant experimental section from Dr. Robello's dissertation.

(3) Friedrich, K. *Angew. Chem., Int. Ed. Engl.* **1967**, 6, 959.

(4) Professor Moore's group apparently also had some difficulty in reproducibly obtaining good yields of C but have improved the method and will report their results in a forthcoming full paper; private communication from J. A. Moore (see ref 2, above).

(5) Shi and Wudl (Shi, S.; Wudl, F.) have observed that a polymeric diaminodicyanoethylene, analogous to **5** was obtained from **4** and *p*-phenylenediamine; unpublished, manuscript in preparation.

(6) Hibbert, F.; Hunte, K. P. P. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1995.

(7) Albert, A.; Ritchie, B. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 53 (note 9).

(8) Dr. Anthony W. Czarnik (Ohio State University) suggested to us that "the tetramethyl compound is not likely to be basic at the heterocyclic nitrogen, as the dimethylamino group will likely be orthogonal to the aromatic ring...; however, it may be unusually basic at the exocyclic amine site in much the same way that tetramethyl orthophenylenediamine is". Dr. Czarnik's statement is based on findings of his group that 9,10-diaminoanthracene is a considerably better electron donor than its *N*,*N*,*N*′,*N*′-tetramethyl derivative (Chung, Y.-S.; Duerr, B. F.; Nanjappan, P.; Czarnik, A. W. *J. Org. Chem.*, in press. We thank Dr. Czarnik for a prepint copy forwarded to us).

0022-3263/88/1953-5379$01.50/0 © 1988 American Chemical Society