Indeed, after desilylation with TBAF and palladium-catalyzed hydrogenolytic cleavage of the benzyl group, specionin (**2d**) was isolated in 90% yield.[19]

In summary, specionin has been prepared in about 18 steps from 7α. Six of the seven stereogenic centers have been introduced with complete stereocontrol; only in the case of introduction of the C-6 hydroxyl group is a mixture obtained in which the desired isomer predominates (3/1). The synthesis serves to confirm the structural assignment of specionin which has recently been made by Vandewalle and co-workers. More importantly, it should provide a general entry into iridoid aglucones of the catalpol type, and it is easily envisioned that many other related molecules could be prepared with the highly oxygenated intermediates already in hand.[20]

Acknowledgment. We thank the National Institutes of Health (GM-31678) for funding of this work. We also thank Professor M. Vandewalle for a friendly exchange of samples, spectra, and unpublished results.

(19) Our synthetic specionin was identical in all respects with a sample kindly provided by Professor Nakanishi via Professor Vandewalle. The optical rotation of specionin has apparently not been reported. We find that natural specionin exhibits an $[\alpha]^{25}_D = -30.7$, *c* 0.08, $CHCl_3$. Our synthetic specionin: $[\alpha]^{25}_D = -29.5$, *c* 0.30, $CHCl_3$; ^{13}C NMR ($CDCl_3$) δ 15.1, 15.3, 29.1, 33.1, 40.3, 60.6, 61.2, 63.1, 63.9, 66.6, 79.0, 93.8, 96.1, 115.3, 122.2, 132.2, 160.4, 166.6; (CD_3OD) δ 15.5, 15.6, 30.3, 34.2, 41.2, 61.2, 61.4, 64.0, 64.8, 67.3, 80.7, 94.9, 97.8, 116.2, 122.0, 133.0, 163.8, 168.3.

(20) All intermediates described in Scheme II have been fully characterized. A forthcoming full paper will describe in detail the synthesis of specionin as well as the preparation of isomers **2a** and **2b** and the synthesis of ethyl catalpol.

Kinamycin Biosynthesis. Derivation by Excision of an Acetate Unit from a Single-Chain Decaketide Intermediate

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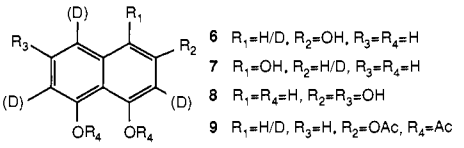
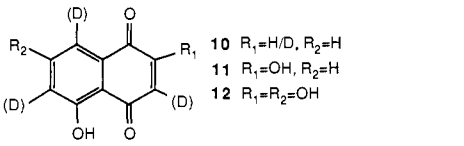
Received March 16, 1987

We have previously reported[2,3] on the incorporation of a variety of labeled acetates during the biosynthesis of the kinamycin antibiotics,[4-7] produced by *Streptomyces murayamaensis* ATCC 21414. Incorporation of sodium [1,2-$^{13}C_2$]acetate, **1**, established the polyketide nature of the kinamycin skeleton, as shown in Scheme I for kinamycin D, **2**. The labeling pattern was consistent with condensation of two nonsymmetrical intermediates, **3** and **4**, to give a tetracyclic benz[*b*]carbazole **5**. We now report unsuccessful efforts to support this hypothesis, the structure of a newly characterized metabolite of the same organism, and direct proof that this is a key intermediate in kinamycin biosynthesis from a single decaketide precursor.

Polyhydroxynapthalenes **6**,[8,9] **7**,[10,11] and **8**[12] as well as the acetate[13] **9** of **6** and naphthoquinones **10**,[14] **11**,[15] and **12**,[16,17] were



6 R_1=H/D, R_2=OH, R_3=R_4=H
7 R_1=OH, R_2=H/D, R_3=R_4=H
8 R_1=R_4=H, R_2=R_3=OH
9 R_1=H/D, R_3=H, R_2=OAc, R_4=Ac



10 R_1=H/D, R_2=H
11 R_1=OH, R_2=H
12 R_1=R_2=OH

synthesized to test as potential biosynthetic intermediates with isotope dilution experiments involving feedings with sodium [2-^{14}C]acetate. Five of these, **6**, **7**, and **9**-**11**, were also synthesized with deuterium labels to be used for direct feeding experiments.

Each of the deuteriated compounds was fed in multiple pulses to cultures[18] of *S. murayamaensis*, and the derived samples of **2** were analyzed by ^2H NMR.[19] Juglone, **10**, was toxic to the organism. In no case was deuterium incorporation into **2** observed.[20] In the isotope dilution experiments, no radioisotope was trapped by any of the test compounds.

Concomitant with these studies, we further investigated the structures of other colored metabolites of this organism. A crude fraction containing four of these as well as kinamycins and murayaquinone[21] was isolated from 7 L of a 26-h production broth.[22] These were separated by chromatography on Silicar CC-4[23] and elution with CH_2Cl_2. A green metabolite was eluted first and was recrystallized from CH_2Cl_2/hexane to afford dark green needles (26 mg), which proved to be a known compound, **13**,[24] previously

(1) Career Development Awardee of the National Cancer Institute (Grant CA-00880), 1979-1984.

(2) Sato, Y.; Gould, S. J. *Tetrahedron Lett.* **1985**, *26*, 4023.

(3) Sato, Y.; Gould, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 4625.

(4) Ito, S.; Matsuya, T.; Omura, S.; Otani, M.; Nakagawa, A.; Iwai, Y.; Ohtani, M.; Hata, T. *J. Antibiot.* **1970**, *23*, 315.

(5) Hata, S.; Omura, S.; Iwai, Y.; Nakagawa, A.; Otani, M. *J. Antibiot.* **1971**, *24*, 353.

(6) Omura, S.; Nakagawa, A.; Yamada, H.; Hata, T.; Furusaki, A.; Watanabe, T. *Chem. Pharm. Bull.* **1973**, *21*, 931.

(7) Sato, Y.; Geckle, M.; Gould, S. J. *Tetrahedron Lett.* **1985**, *26*, 4019.

(8) For the natural occurrence of **6** and **11**, see: (a) Stipanovic, R. D.; Bell, A. A. *Mycologia* **1977**, *69*, 164, (b) Tokousbalides, M. C.; Sisler, H. D. *Pestic. Biochem. Physiol.* **1979**, *11*, 64.

(9) Synthesis of **6** followed the procedure described in the following: Cameron, D. W.; Feutrill, G. I.; Pannan, L. J. H. *Aust. J. Chem.* **1980**, *33*, 2531. Deuterium was introduced by direct exchange of **6** in D_2O/OD^-.

(10) For the natural occurrence of **7** and **10**, see: Mueller, W. H.; Leistner, E. *Phytochemistry* **1978**, *17*, 1735.

(11) **7** was synthesized from juglone (**10**)[15] as described in the following: Thomson, R. H. *J. Chem. Soc.* **1950**, 1737.

(12) Biosynthesis of **2** must proceed through nonsymmetrical intermediates.[3] **8** was synthesized as a negative control for isotope dilution experiments as described by the following: Bycroft, B. W.; Cashyap, M. M.; Leung, T. K. *J. Chem. Soc., Chem. Commun.* **1974**, 443.

(13) Acetate **9** was obtained by reaction of **6** with Ac_2O/pyridine. Spectral properties were identical with those reported by the following: Findlay, J. A.; Kwan, D. *Can. J. Chem.* **1973**, *51*, 1617.

(14) Synthesis of **10** from 1,5-dihydroxynaphthalene is described by the following: Wakumutsu, T.; Nishi, T.; Ohnuma, T.; Ban, Y. *Synth. Commun.* **1984**, *14*, 1617. Deuterio-1,5-dihydroxynaphthalene (obtained by exchange in D_2O/OD^-) was used to generate deuterio-**10**.

(15) **11** was synthesized from juglone as described in the following: Thomson, R. H. *J. Org. Chem.* **1951**, *16*, 1082.

(16) For natural occurrence of **12**, see: Sankawa, U.; Shimada, H.; Sato, T.; Kinoshita, T. *Tetrahedron Lett.* **1977**, 483.

(17) **12** was synthesized from **8** as described in the following: Baker, P. M.; Bycroft, B. W. *J. Chem. Soc., Chem. Commun.* **1968**, 71.

(18) Production cultures (200 mL; 2% glycerol, 0.1% K_2HPO_4, 0.1% asparagine, 0.04% $MgSO_4$, 0.01% $FeSO_4$) were innoculated with 10 mL of a 48-h seed culture[3] of *S. murayamaensis*.

(19) ^2H NMR were taken on a Bruker AM 400 spectrometer at 61.4 MHz by using a 5-mm probe with broad band proton decoupling.

(20) **6** and **7** were partially oxidized to the quinones; **9** was recovered unchanged, and symmetrical tetrol **8** was totally oxidized to flaviolin (**12**) by production cultures. Neither **8** nor **12** are metabolites of *S. murayamaensis*.

(21) Sato, Y.; Kohnert, R.; Gould, S. J. *Tetrahedron Lett.* **1986**, *27*, 143.

(22) Production broth (7 L) (3% glycerol, 0.13% $(NH_4)_2SO_4$, 0.1% K_2HPO_4, 0.04% $MgSO_4$, 0.01% $FeSO_4$, and 0.2% $CaCO_3$) in a 14-L vessel (New Brunswick Scientific Microferm stirred fermentor) was innoculated with 200 mL of a 48-h seed culture and incubated at 25-26 °C, 300 rpm, 10 L/min aeration. Upon acidification of the 26-h broth, the mycelia floated to the surface allowing for the broth to be siphoned off, and the remaining cell suspension was sonicated. The broth and cell suspension were combined, extracted with toluene, and concentrated to a brown residue (930 mg) which contained the green, purple, and yellow pigments as well as the kinamycins and murayaquinone.

(23) Silicar CC-4 was obtained from Mallinkrodt (7086).

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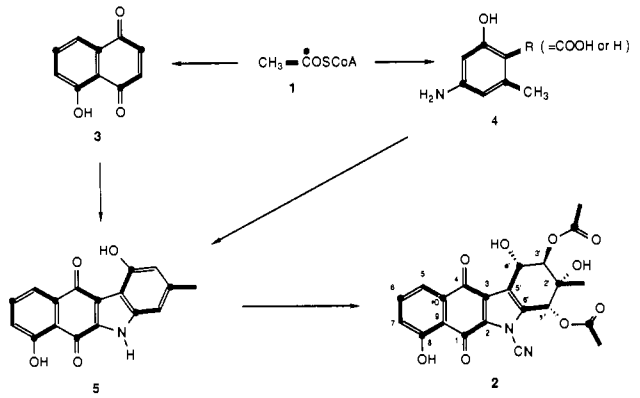
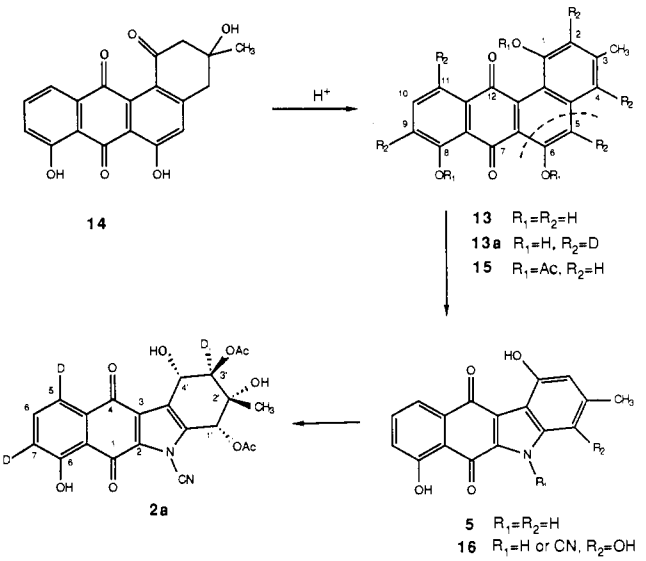
Scheme I



Scheme II



obtained from the acid-catalyzed dehydration of rabelomycin, **14**.[25] This was corroborated by conversion to the triacetate **15**[26] with acetic anhydride/concentrated H_2SO_4. A subsequent, milder workup still yielded only **13** and no **14**, ensuring that **13** is not an artifact.

The formation of **13** by *S. murayamaensis* suggested an alternate biosynthesis (Scheme II) to that shown in Scheme I. A sample of **13** was heated in deuteriotrifluoroacetic acid at 100 °C in a sealed tube under nitrogen for 48 h; workup gave a 50% yield of [2,4,5,9,11-$^2H_5$]dehydrorabelomycin, **13a** (64% deuteriated at C-9 and 82–90% deuteriated at the other four positions). Twelve mg of **13a** was fed in 6-mg portions at 12 and 18 h after inoculation, each portion being divided between three 200-mL production broths. At 26 h the fermentation was terminated. Workup afforded 8 mg of recovered **13a**, unchanged in deuterium content, and 15 mg of **2a**. ^2H NMR analysis (61.4 MHz, acetone, dioxane for chemical shift reference and deuterium quantification) of the latter showed resonances at δ 7.51, 7.17, and 5.51, corresponding to C-7, C-5, and C-3′, respectively (average enrichment, 4.6%).

This result establishes **13** as a key intermediate in the biosynthesis of **2**. As shown in Scheme II, cyclization of a decaketide to **13**, followed by oxidative cleavage of the C-ring and excision of carbons C-5 and C-6—representing a single precursor acetate unit—and insertion of nitrogen would yield a tetracyclic benz[*b*]carbazole **5**.[27] In addition, our original hypothesis[3] for the intermediacy of hydroquinone **16** is fully consistent with the observed retention of deuterium at C-3′ but not at C-1′ of **2**.[28]

Recently, numerous benz[*a*]anthraquinones have been reported from *Streptomyces* and *Norcardia* species.[29] The fracture of this ring system and excision of a two-carbon fragment in the biosynthesis of the kinamycins represents a novel polyketide metabolism. While cleavage of an aromatic ring and oxidative removal of one carbon is quite common,[30] only two previous examples involving apparent loss of a two-carbon unit have been reported.[31] Work on the structures of the other colored metabolites of *S. murayamaensis* is continuing.

Acknowledgment. This work was supported by U.S. Public Health Service Grant GM-31715 to S.J.G. Professor S. Ōmura of Kitasato University is thanked for a culture of *S. murayamaensis* and for a sample of kinamycin D. The multinuclear Bruker AM 400 NMR spectrometer was purchased in part through grants from the National Science Foundation (CHE-8216190) and from the M. J. Murdock Charitable Trust to Oregon

(24) **13**: mp 201–203 °C (lit.[25] mp = 204–205 °C); UV ($CHCl_3$) 249.2, 272.0, 324.4, 470.0, 597.6 nm; IR (KBr) 3438, 2922, 1635, 1603, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 12.12 (s, 1 H), 11.77 (s, 1 H), 10.31 (s, 1 H), 7.84 (d, J = 8.3 Hz, 1 H), 7.72 (t, J = 8.3 Hz, 1 H), 7.65 (s, 1 H), 7.33 (d, J = 8.5 Hz, 1 H), 7.02 (s, 1 H), 6.88 (s, 1 H); ^{13}C NMR ($CDCl_3$, 40 °C, 10-mm tube) 193.2, 189.1, 162.0, 154.6, 142.8, 141.6, 137.6, 135.1, 132.8, 128.3, 125,1, 124.0, 121.5, 119.7, 119.6, 118.4, 118.3, 114.8, 21.0 ppm.

(25) Liu, W. C.; Parker, W. L.; Slusarchyk, D. F.; Greenwood, G. L.; Graham, S. F.; Meyers, E. *J. Antibiot.* **1970**, *23*, 437.

(26) **15**: mp 237–239 °C; UV ($CHCl_3$) 253.6, 296.0, 337.6, 363.2 nm; IR (KBr) 2920, 1773, 1672, 1365, 1285, 1193 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91 (dd, J = 1.1, 7.7 Hz, 1 H), 7.75 (t, J = 7.8 Hz, 1 H), 7.66 (s, 1 H), 7.50 (s, 1 H), 7.37 (dd, J = 1.0, 8.0 Hz, 1 H), 7.32 (d, J = 1.5 Hz, 1 H), 2.55 (s, 3 H), 2.47 (s, 3 H), 2.46 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) 185.1, 180.5, 169.8, 169.3, 168.5, 149.3, 146.9, 145.5, 141.0, 137.8, 136.6, 136.1, 134.7, 129.0, 127.0, 126.7, 125.7, 124.8, 123.7, 119.8, 21.6, 21.13, 21.10, 21.0 ppm; MS m/z (rel abundance) 446 (9, M^+ = $C_{24}H_{18}O_8$), 404 (33, M-$C_2H_2O^+$), 362 (20, M-$C_4H_4O_2^+$), 320 (100, M-$C_6H_6O_3$); HRMS (70 eV) m/z calcd for $C_{25}H_{18}O_8$ 446.0996, found 446.10013.

(27) Although not complete, spectroscopic data indicated that one of the purple compounds, obtained in only small quantities, is *N*-cyano-**5**.

(28) The structural similarity of the D-ring of **2** with the C-ring of altersolanol A [(a) Stoessl, A. *Can. J. Chem.* **1969**, *47*, 777. (b) Gordon, M.; Stoessl, A.; Stothers, J. B. *Can. J. Chem.* **1972**, *50*, 122.] appears not to be biogenetically relevant since labeling data suggest that in the latter case [Stoessl, A.; Unwin, C. H.; Stothers, J. B. *Can. J. Chem.* **1983**, *61*, 372.] hydroxylation at the position corresponding to C-1′ of **2** takes place at a nonaromatic, benzylic position.

(29) (a) Tetrangomycin and tetrangulol: Kuntsmann, M. P.; Mitscher, L. A. *J. Org. Chem.* **1966**, *31*, 2920. (b) Ochromycinone: Bowie, J. H.; Johnson, A. W. *Tetrahedron Lett.* **1967**, 1449. (c) Aquamycin: Sezaki, M.; Kondo, S.; Maeda, K.; Umezawa, H.; Ohno, M. *Tetrahedron* **1970**, *26*, 5171. (d) X-14881 A-D: Maehr, H.; Lie, C.; Liu, M.; Perrotta, A.; Smallheer, J. M.; Williams, T. H.; Blount, J. F. *J. Antibiot.* **1982**, *35*, 1627. Blount, J. F.; Greeley, D. N.; Maehr, H.; Perrotta, A.; Pitcher, R. G.; Todaro, L.; Williams, T. H. *J. Antibiot.* **1985**, *38*, 1270, 1272. (e) Sakomycin, A-D; Irie, H.; Misuno, Y.; Tagasawa, T.; Kouno, I.; Tani, Y.; Yamada, H.; Taga, T.; Osaki, K. *J. Chem. Soc., Chem. Commun.* **1983**, 174. Nagasawa, T.; Fukao, H.; Irie, H.; Yamada, H. *J. Antibiot.* **1984**, *37*, 693. (f) PD 116740: Wilton, J. H.; Cheney, D. C.; Hokanson, G. C.; French, J. C. *J. Org. Chem.* **1985**, *50*, 3936. (g) Saquayamycins: Uchida, T.; Imoto, M.; Watanabe, Y.; Miura, K.; Dobashi, T.; Matsuda, N.; Sawa, T.; Nagawana, H.; Hamada, M.; Umezawa, H. *J. Antibiot.* **1985**, *38*, 171. (h) Funjianmycins: Rickards, R. W.; Wu, J. P. *J. Antibiot.* **1985**, *38*, 513. (i) Capoamycin: Hayakawa, Y.; Iwakiri, T.; Imarara, K.; Seto, H.; Otake, N. *J. Antibiot.* **1985**, *38*, 957. (j) Benzanthrins, A and B: Therialt, R. J.; Rasmussen, R. R.; Kohl, W. L.; Prokop, J. H.; Hutch, T. B.; Barlow, G. J. *J. Antibiot.* **1986**, *39*, 1509. Rasmussen, R. R.; Nuss, M. E.; Scherr, M. H.; Mueller, S. L.; McAlpine, J. B. *J. Antibiot.* **1986**, *39*, 1515. (k) Urdamycins: Drautz, H.; Zahner, H.; Rohr, J.; Zeeck, A. *J. Antibiot.* **1986**, *39*, 1657. (l) Kerriamycins A–C: Hayakawa, Y.; Furihata, K.; Seto, H.; Otake, N. *Tetrahedron Lett.* **1985**, *26*, 3475.

(30) (a) Aflatoxin B_1 via averufin and sterigmatocystin: Pachler, K. G. R.; Steyn, P. S.; Vleggaar, R.; Wessels, P. L.; Wright, J. L. C. *J. Chem. Soc., Chem. Commun.* **1975**, 66. (b) Aspyrone: Brereton, R. G.; Garson, M. J.; Staunton, J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1027. (c) Lambertellin via chrysophanol: Brown, P. M.; Krishnamoorthy, V.; Mathieson, J. W.; Thomson, R. H. *J. Chem. Soc. C* **1970**, 109. (d) Terrein: Hill, R. A.; Carter, R. H.; Staunton, J. *J. Chem. Soc., Chem. Commun.* **1975**, 380. (e) Ligustrone A: Assante, G.; Locci, R.; Camarda, L.; Merlini, L.; Nasini, G. *Phytochem.* **1977**, *16*, 243. (f) Mollisin: Casey, M. L.; Paulick, R. C.; Whitlock, H. W. *J. Am. Chem. Soc.* **1976**, *98*, 2636. (g) Ravenelin via icelandicin: Birch, A. J.; Baldas, J.; Hlubucek, R.; Simpson, T. J.; Westerman, P. W. *J. Chem. Soc., Perkin Trans. 1* **1976**, 898.

(31) (a) Chartreusin biosynthesis: Canham, P.; Vining, L. C. *Can. J. Chem.* **1977**, *55*, 2450. (b) α-Naphthocyclinone biosynthesis: Krone, B.; Zeeke, H. *J. Org. Chem.* **1982**, *47*, 4721.

State University. The high resolution mass spectrum was obtained on a Kratos MS 50 TC spectrometer purchased with grants from the National Institutes of Health Division of Research Resources (DRR-1S10RR01409) and from the Anheuser-Busch Company.

The 2,3-Dimethylenecyclohexa-1,3-diene Diradical Is a Ground-State Triplet

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Received April 27, 1987

The properties of the tetramethyleneethane diradical (I) form the focal point of an intense conflict that has developed between theory and experiment.[1,2]

I II

Since tetramethyleneethane (I) is a disjoint conjugated system, it has been suggested[3,4] on qualitative grounds that the singlet state is the preferred ground state. Disjoint conjugation has provided a basis for understanding the ground-state multiplicity of cyclobutadiene,[4] which adopts a ground singlet state. If the singlet ground state found for cyclobutadiene is due to a lifting of the orbital degeneracy by a rectangular distortion, there is a smaller probability that Hund's rule will be violated by non-Kekulē hydrocarbons, since by definition, such molecules lack one covalent bond and afford less opportunity for covalent bonding in the singlet state than is possible in a Kekulē molecule such as cyclobutadiene.

We recently established that the parent tetramethyleneethane (I) is a ground-state *triplet*, since it yields a linear Curie law plot.[1] Tetramethyleneethane (I) may be viewed in steric terms as a truncated biphenyl; it probably adopts a twisted conformation, and the two halves may even be canted perpendicular to one another (D_{2d}). It seemed probable that the disagreement between theory and experiment had arisen, because we had observed the perpendicular or twisted conformation of tetramethyleneethane (I), while the theoretical work was focused on the planar conformation. However, Du and Borden[2] have recently carried out further calculations and concluded that tetramethyleneethane (I) should be a *ground-state singlet at all conformations*—irrespective of the angle of twist about the central carbon-carbon bond.

In view of this challenge, it was important to examine other conformations, and the diradical II with tetramethyleneethane incorporated into a six-membered ring was available from the work of Roth.[5] With four sp^2-hybridized carbon atoms in a six-membered ring, II is very close to being a planar system. We estimate, using an MM2 procedure,[6] that diradical II deviates from planarity by less than 5°. Accordingly, II becomes an attractive subject for Curie law analysis.

Comparison of the spectrum of tetramethyleneethane (I) with its derivative II is revealing. The tetramethyleneethane (I) spectrum shows no splitting between the x and y lines, a result consistent with the twisted or D_{2d} symmetry. The spectrum of the diradical II differs significantly from that of I. With a D value of 0.024 cm^{-1}, the spectrum is in good agreement with that expected for a tetramethyleneethane (for I, D = 0.025 cm^{-1})[7]. However, the E value of II is 0.0037 cm^{-1}, as expected for a diradical with planar symmetry. The appearance of the latter (Figure 1) supports the idea that diradical I is not planar.

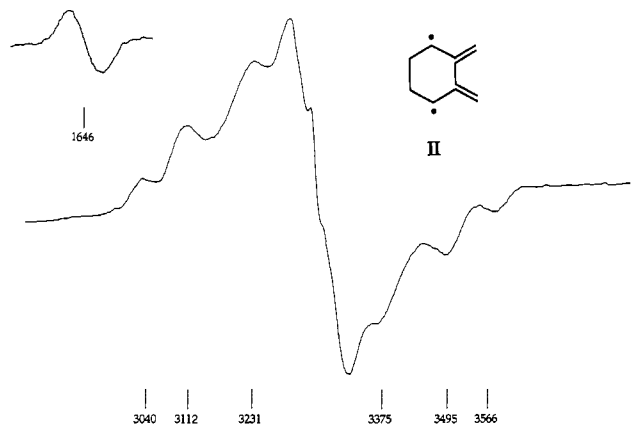

Figure 1. Electron spin resonance spectrum (Δm = 1 lines) of the 2,3-dimethylenecyclohexa-1,3-diene diradical (II). The Δm = 2 line is shown in the inset.

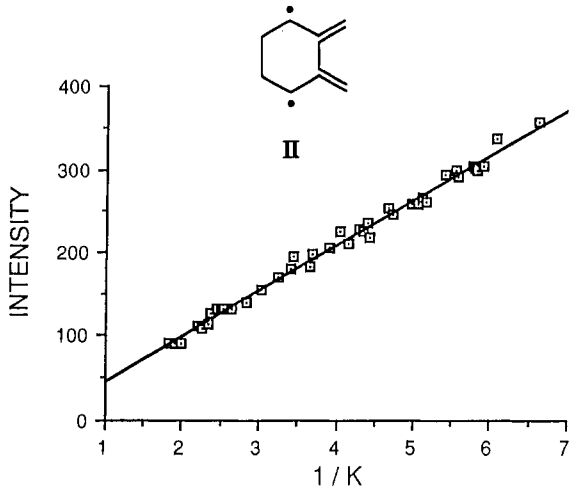

Figure 2. Curie–Weiss plot (least squares, r = 0.996) of the signal intensity of the Δm = 2 line of the 2,3-dimethylenecyclohexa-1,3-diene diradical (II). The temperature range was 15–53 K; the solvent was 2-methyltetrahydrofuran.

A Curie law plot of the intensity of the Δm = 2 line of II vs. temperature from 15–53 K (Figure 2) is linear with a correlation coefficient of 0.996. We conclude that *the planar tetramethyleneethane diradical II is a ground-state triplet.*[10]

It is widely appreciated[8,9] that if the singlet and triplet states are degenerate within 30–40 cal, then a linear Curie law plot will be observed. We estimate that if the singlet and triplet states differ

(1) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416.
(2) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 930.
(3) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4487.
(4) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 1–72.
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(7) The reported D and E values of 0.0204 and 0.00159 are slightly different from those we have observed. We observe Δm = 1 lines at 3040, 3112, 3231, 3375, 3495, and 3566 with the Δm = 2 line at 1646 G (microwave frequency 9.256 GHz) following photolysis in a methyltetrahydrofuran matrix at 15 K. The center of the Δm = 1 spectrum is somewhat obscured by a large monoradical impurity.
(8) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 217.
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(10) Another example of a non-Kekulē molecule whose ground-state multiplicity is at odds with theoretical expectation is provided by the recent work of Roth, W. R.; Langer, R.; Bartmann, M.; Steverman, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 256.

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