crystallization from MeOH: mp >250 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.77 (br s, 1 H), 8.28 (d, J = 5.4 Hz, 1 H), 8.24 (s, 1 H), 6.83 (d, J = 5.4 Hz, 1 H), 3.53 (s, 2 H); IR (KBr disc) 1712, 1619, 1597, 1488 cm^{-1}; MS m/z (relative percent) 134 (100), 106 (22), 105 (34). Anal. Calcd for $C_7H_6N_2O$: C, 62.68; H, 4.51; N, 20.88. Found: C, 62.28; H, 4.47; N, 20.72.

Unusual, Cofacial Structure of a Sterically Congested Stilbene: (*Z*)-2,2,5,5-Tetramethyl-3,4-diphenyl-3-hexene

James E. Gano,* Bong-Ser Park, and Girija Subramaniam

Department of Chemistry, University of Toledo, Toledo, Ohio 43606

Dieter Lenoir

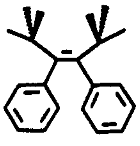
GSF Research Center, Institute of Ecological Chemistry, Ingolstaedterstr 1, D-8044 Neuherberg, Germany

Rolf Gleiter

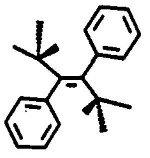
Organisch Chemisches Institut, University of Heidelberg, 6900 Heidelberg 1, West Germany

Received February 11, 1991

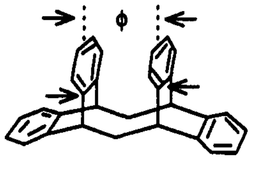
The unusual steric effects and "one-way photoisomerizations" reported in naphthalenes prompted an investigation of the related sterically congested stilbenes, (*Z*)- (1) and (*E*)-2,2,5,5-tetramethyl-3,4-diphenyl-3-hexene (2).[1-3] In order to understand the observed low isomerization barrier and spectra,[2f] a further investigation of 1 and 2 is now reported. X-ray structural analysis, photoelectron (PE) spectroscopy, and theory elaborates the unique structures of 1 and 2 described in the following text.



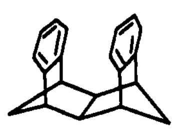
1



2



3



4

The properties of 1 and 2 gave hints to unusual structures.[2f] Both had UV spectra more like toluene than stilbenes (e.g., 2 showed λ = 262, 235 sh, 207 max, ϵ = 1.1 × 10^4). The ^{1}H NMR spectrum of 2 showed an upfield-shifted *tert*-butyl resonance at δ 0.7 and normal aromatic signals, whereas the ^{1}H NMR spectrum of 1 showed upfield shifted aromatic resonances at δ 6.6–6.9 and normal *tert*-butyl signals.

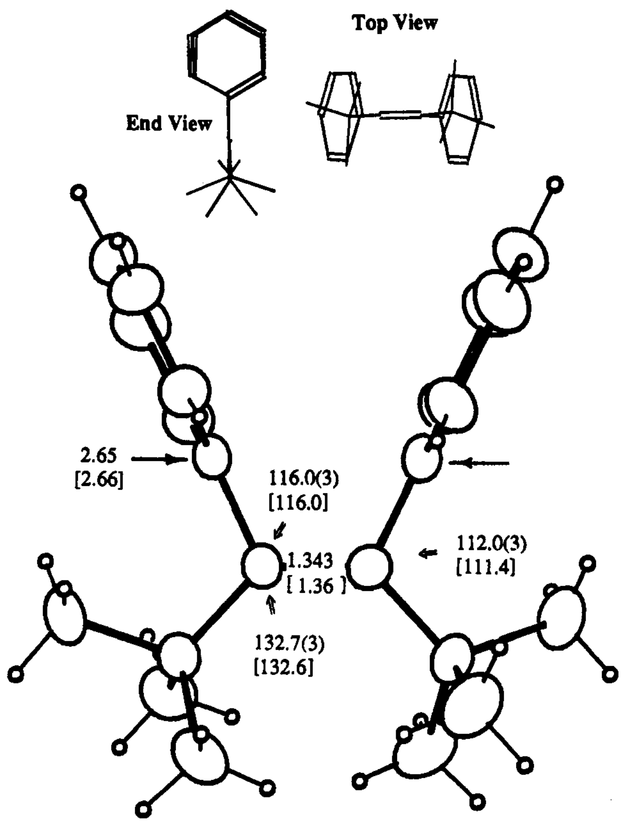


Figure 1. Drawings of X-ray crystal structure of 1. Values in brackets calculated by AM1.

X-ray analysis of 1, crystallized from methanol, clearly showed (Figure 1) no twisting about the central double bond in contrast to (*Z*)-stilbene.[4-6] Instead, the planes of the phenyl groups are perpendicular to the plane of the central C=C bond. The π-systems of the phenyl rings are cofacial or "face-to-face" to one another and orthogonal to the central π-bond.[7] As has been seen in other cases,[8b] this compression of the phenyl rings did not affect the ring planarity in 1. The dominant distortion is the mutual repulsion of the *tert*-butyl groups to open the *t*-Bu—C=C angle to 132.7° and compress the phenyl rings.

Comparison to related cofacial hydrocarbons, including 3 and 4, reveals 1 to be unique with the (a) absence of a

---

(1) For a general review of alkene isomerizations, see: Saltiel, J.; Charlton, J. L. In *Rearrangements in the Ground and Excited States*; DeMayo, P., Ed.; Academic: New York, 1980; p 25.

(2) For related papers see: (a) Lenoir, D.; Malwitz, D.; Meyer, B. *Tetrahedron Lett.* **1984**, *25*, 2965. (b) Gano, J. E.; Eizenberg, L. *J. Am. Chem. Soc.* **1973**, *95*, 972. (c) Chapman, O. L.; Gano, J. E.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033. (d) Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. *J. Am. Chem. Soc.* **1982**, *104*, 2326. (e) Mueller, P. H.; Houk, K. N.; Gano, J. E.; Platz, M. S. *Tetrahedron Lett.* **1983**, 485. (f) Lenoir, D.; Gano, J. E.; McTague, J. A. *Tetrahedron Lett.* **1986**, *27*, 5339.

(3) Hamaguchi, H.; Tasumi, M.; Karatsu, T.; Arai, T.; Tokumaru, K. *J. Am. Chem. Soc.* **1986**, *108*, 1698. (b) Arai, T.; Karatsu, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1983**, *24*, 2873.

(4) Details of X-ray: Gano, J. E.; Subramaniam, G.; Pinkerton, A. A.; Birnbaum, R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, submitted for publication.

(5) Partial X-ray structure: Ermer, O. *Z. Naturforsch., Teil B* **1977**, *32*, 837.

(6) MMP2 of 2: Favini, G.; Simonetta, M.; Sottocornola, M.; Todeschini, R. *J. Comput. Chem.* **1982**, *3*, 178.

(7) Although "face-to-face" has been used to describe this relationship, which is clearly not coplanar, the succinct term cofacial is preferred by the current authors.

(8) **Janusenes 3**: (a) Cristol, S. J.; Lewis, D. C. *J. Am. Chem. Soc.* **1967**, *89*, 1476. (b) MacIntyre, W. M.; Tench, A. H. *J. Org. Chem.* **1973**, *38*, 130. **[3,3]Orthocyclophanes 5**: (c) Mataka, S.; Takahashi, K.; Hirota, T.; Takuma, K.; Kobayashi, H.; Tashiro, M. J. *J. Chem. Commun.* **1985**, 983. (d) Mataka, S.; Takahashi, K.; Mimura, T.; Hirota, T.; Takuma, K.; Kobayashi, H.; Tashiro, M. J. *J. Org. Chem.* **1987**, *52*, 2656. **4** (structure in text): (e) Fessner, W.-D.; Sedelmeier, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626. (f) Prinzbach, H.; Sedelmeier, G.; Krüger, C.; Goddard, R.; Martin, H.-D.; Gleiter, R. *Angew. Chem., int. Ed. Engl.* **1978**, *17*, 271. **Hypostrophenes 6**: (g) Fessner, W.-D.; Sedelmeier, G.; Knothe, L.; Prinzbach, H.; Rihs, G.; Yang, Z.-Z.; Kovac, B.; Heilbronner, E. *Helv. Chim. Acta* **1987**, *70*, 1816.

0022-3263/91/1956-4806$02.50/0 © 1991 American Chemical Society

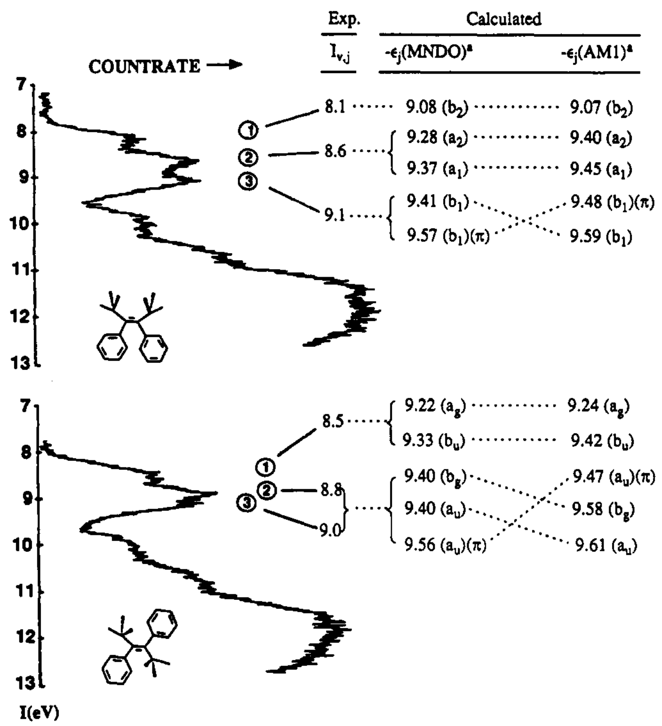


Figure 2. He(I) PE spectra of 1 and 2 and comparison between the recorded vertical ionization energies, I_{vj}, and calculated orbital energies, ϵ_j, of the π-MO's. All values in eV.

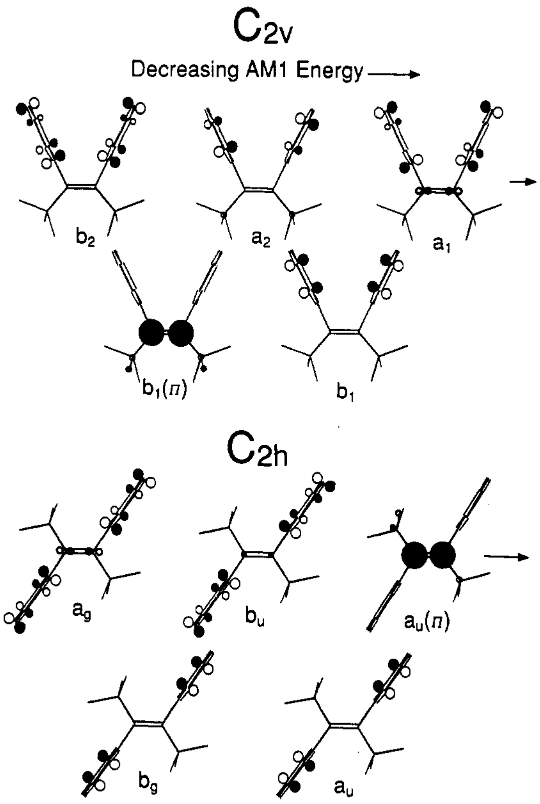


Figure 3. Schematic drawings of the occupied π-MO's of 1 and 2 as calculated by AM1. Labels assume C_{2v} and C_{2h} symmetry, respectively. Circle sizes approximately proportional to eigenvectors.

rigid skeleton to maintain its *Z* geometry, (b) absence of a rigid skeleton to restrict phenyl rotation, (c) presence of a double bond available for electronic interaction *but sterically inaccessible for chemical reaction*, and (d) closest ring–ring approach.[8,9] The 2.65-Å ipso–ipso separation is well below the 3.4-Å van der Waals distance for aromatic rings. An interring interaction would be expected in 1 that would be absent in 2. The nature and significance of this interaction was investigated with PE spectroscopy and semiempirical theoretical methods.

The PE spectra of 1 and 2 are shown in Figure 2. For 1, three peaks are evident below 9.5 eV, while in the case of the PE spectrum of 2 only two peaks and a shoulder can be recognized in the low-energy region. The ratio of areas below the peaks amounts approximately to 1:2:2 for 1 and 2:3 for 2. Furthermore, both spectra are different with respect to the half-height width if bands 1–3 are considered. For 1 we find a half-height of 1.4 eV and for 2 1.1 eV. From PE studies on (*Z*)- and (*E*)-stilbene[9,10] and substituted ethylenes,[11] it seems reasonable to assign the first peaks to the ionization events from the olefinic π-bond, $b_1(C_{2v})$ or $a_u(C_{2h})$, and the corresponding linear combinations from the former e_S and e_A MO's of the two benzene units. As an example, we show these combinations for 1 and 2, as calculated by AM1, in Figure 3. To check the empirical assignment of the first peaks mentioned previously we have carried out semiempirical calculations using the MNDO[12] and the AM1[13] methods. Both procedures predicted similar geometries, and the five π-MO's mentioned previously were well separated from the others as found in the PE spectra. *AM1, the preferred method*[13a], *positioned the central π-bonds* (*Figure 2*) *higher in energy.* If we adopt the validity of Koopman's theorem (vertical ionization energy, I_{vj}, = −orbital energy, ϵ_j),[14] we find that both methods overestimate the ionization energy by 1 eV. The larger spread of the bands in 1 (1.0 eV) as compared to 2 (0.5 eV) is underemphasized by the calculations. Nevertheless, the larger split of the highest occupied MO's in the case of 1 as compared to 2 is shown to be due to the strong through-space interaction of the cofacial benzene rings. The energy difference between b_2 and a_1 in 1 is calculated to be 0.3–0.4 eV while the corresponding split calculated for 2 was found to be 0.1–0.2 eV with a_g moved above b_u due to a weak through-bond interaction with the σ-bond of the central unit. In addition, the energy difference between a_2 and b_1 in 1 is calculated to be 0.1–0.2 eV, while the corresponding split in 2 was found to be 0.0 eV. Consequently, the strong through-space interaction and the very weak through-bond interaction for the benzene e_S linear combination in 1 rationalizes the lower ionization energy of the first band and the higher ionization energy of the last band, leading to the larger half-height width of bands 1–3 as compared to those in 2. The lowest energy ionization from 1 (8.1 eV) is 0.4 eV below that observed in 2. That reveals an interring interaction comparable to that reported for 4[8e,f]. The closer approach of the ipso position in 1 apparently compensates for the re-

---

[9] (a) Anthracene photodimer 7: Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342. (b) Although 5 showed a [6+6] photocyclization, no ring–ring photochemistry was observed for 1.

[10] (a) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1784. (b) Kobayashi, T.; Suzuki, H.; Ogawa, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1734.

[11] (a) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo, 1981. (b) Mollere, P. H.; Houk, K. N.; Bomse, D. S.; Morton, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 4732.

[12] Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

[13] (a) Although the most recently developed PM3 protocol might seem to be the method of choice, *it failed to predict the important features observed in the PE spectra of 1 and 2*. (b) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[14] Koopmans, T. *Physica* **1934**, *1*, 104.

[15] Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

duced orbital overlap in the meta and para positions, compared to 4, caused by the wider angle between the rings.

The calculated (AM1) geometry of 1 matched well with the X-ray structure as seen by the values in Figure 1. Of particular interest were the central C=C distance (1.343 (5) vs 1.36 Å (calcd)) and the C_{ipso}—C_{ipso} distance (2.65 vs 2.66 Å calcd).[4]

The toluene-like UV spectrum of 1 is explained by the X-ray structure. The orthogonal rings lacked the typical stilbene conjugation. In contrast to 3 and 4, and despite the 2.65 Å ipso–ipso separation, no appreciable bathochromic shift was observed upon comparison of 1 and 2 to suggest electronic interaction of the rings. AM1 calculations only predicted a 4-nm shift. PES would seem to be a more sensitive test for these effects. The upfield shifted aromatic resonances observed in the ^1H NMR spectrum of 1 were typical of 3 and 4 and are diagnostic of cofacial stilbenes.

Further work to investigate the potential for interring interactions in these systems is in progress.

Acknowledgment. Technical assistance from A. Flatow, J. McTague, and S. Roberts and financial support from the University of Toledo Faculty Research Awards and Fellowship Program, the Ohio Research Challenge Program (J.G.), the College of Arts and Science X-ray Facility, the Deutsche Forschungsgemeinschaft (Grant No. Le 288/14), and the Fonds der Chemischen Industrie (R.G.) are gratefully acknowledged.

Supplementary Material Available: Atomic positions for 1 (1 page). Ordering information is given on any current masthead page.

Base-Catalyzed Hydrogen Exchange and Estimates of the Acid Strength of Benzoyl- and (Trimethylsilyl)acetylene in Aqueous Solution. A Correlation between Acetylene pK_a Estimates and Hydroxide-Ion Catalytic Coefficients for Hydrogen Exchange

A. Jerry Kresge* and Przemyslaw Pruszynski

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Peter J. Stang and Bobby L. Williamson

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received July 13, 1990 (Revised Manuscript Received April 1, 1991)

The proton NMR chemical shift of the acetylenic hydrogen in terminal alkynes would be expected to move downfield as the acidity of this hydrogen increases. The unusually low-field value of the chemical shift for benzoylacetylene, 1, δ = 3.33 ppm,[1] thus suggests that this

$$\underset{\mathbf{1}}{PhC(O)C{\equiv}CH} \qquad \underset{\mathbf{2}}{Me_3SiC{\equiv}CH}$$

substance might be quite acidic. As part of our continuing interest in more strongly acidic acetylenes, we have consequently examined benzoylacetylene for the purpose of estimating its acid strength in aqueous solution. We have also examined (trimethylsilyl)acetylene, 2, in the same way, for the strong deviation it shows from a correlation of rates of hydrogen exchange of other acetylenes[2] suggests that it is fairly acidic as well.

We used a kinetic method to estimate the acidity of these acetylenes. Our method is based upon the fact that simple terminal monoacetylenes, though carbon acids, generally show normal acid behavior,[3] i.e, their uphill ionization reactions are diffusion-controlled processes in which hydron transfer is rapid and reversible and separation of the hydron-transfer products is rate determining (rd), eq 1.[4] In this circumstance, the barrier to recom-

$$RC{\equiv}CH + B \xrightleftharpoons{\text{rapid}} RC{\equiv}C^-{\cdot}HB^+ \xrightarrow{\text{rd}} RC{\equiv}C^- + HB^+ \tag{1}$$

bination of the hydron-transfer products can be estimated, and that can then be combined with rates of hydrogen exchange of the acetylene to provide acetylenic pK_a's.[4a] We determined the required rates of hydrogen exchange by monitoring the loss of radioactivity from tritium-labeled substrates.

Experimental Section

Materials. Benzoylacetylene[5] was made by the Friedel–Crafts benzoylation of bis(trimethylsilyl)acetylene[6] followed by fluoride-ion promoted removal of the remaining trimethylsilyl group.[7] It was labeled with tritium by exchange with tritiated water catalyzed by 2-(2,6-dimethylphenyl)-1,1,3,3-tetramethylguanidine.[8] This base was chosen as the catalyst because of its high basicity and low nucleophilicity.[9] Exchange was effected by allowing a mixture of 450 mg of benzoylacetylene and 100 μL of tritiated water (0.01 Ci g^{-1}), to which just enough dioxane had been added to achieve homogeneous solution, to stand at room temperature for 24 h. This reaction mixture was then poured into 50 mL of 1 M aqueous HCl, the resulting solution was extracted with ether, and the extract was washed with three 20-mL portions of 1 M HCl and was dried with $MgSO_4$. Removal of the ether by evaporation left a brown residue that was purified to a light yellow waxy solid by vacuum sublimation. A control experiment using D_2O in place of tritiated water showed that this procedure replaced the acetylenic proton with deuterium.

(Trimethylsilyl)acetylene (Fluka) was labeled with tritium by treating its lithium salt with tritiated water. The salt was prepared by adding 5.3 mL of a 1.4 M solution of methyl lithium in diethyl ether (Aldrich) to 1.0 mL of (trimethylsilyl)acetylene dissolved in 2.0 mL of diethyl ether. This mixture was stirred at 0 °C for 15 min, and 0.15 mL of tritiated water (0.01 Ci g^{-1}) was then added. The white precipitate of lithium hydroxide that formed was separated, the ether solution was dried with $MgSO_4$, and the labeled acetylene was separated from the ether by distillation. A parallel experiment using D_2O showed that this procedure gave (trimethylsilyl)acetylene labeled in the terminal acetylenic position.

All other materials were best available commercial grades and were used as received.

Kinetics. Rates of loss of tritium from the labeled acetylenes were measured by radiochemical assay of the substrate at appropriate time intervals. Reaction mixtures were prepared in the case of benzoylacetylene by allowing 50-mL portions of aqueous

---

(1) Rosenberg, D.; Drenth, W. *Tetrahedron* 1971, *27*, 3893-3907.

(2) Eaborn, C.; Skinner, G. A.; Walton, D. R. M. *J. Chem. Soc. B* 1966, 989–990.

(3) Eigen, M. *Angew. Chem., Int. Ed. Engl.* 1964, *3*, 1–19.

(4) (a) Lin, A. C.; Chiang, Y.; Dahlberg, D. B.; Kresge, A. J. *J. Am. Chem. Soc.* 1983, *105*, 5380–5386. (b) Kresge, A. J.; Powell, M. F. *J. Org. Chem.* 1986, *51*, (c) 819–822, (d) 822–824. (e) Aroella, T.; Arrowsmith, C. H.; Hojatti, M.; Kresge, A. J.; Powell, M. F.; Tang, Y. S.; Wang, W.-H. *J. Am. Chem. Soc.* 1987, *109*, 7198–7199.

(5) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* 1946, 39–45.

(6) Birkofer, L.; Ritter, A.; Uhlenbrauck, H. *Chem. Ber.* 1963, *96*, 3280–3288.

(7) Stang, P. J.; Fisk, T. E. *Synthesis* 1979, 438–440.

(8) Pruszynski, P. *Can. J. Chem.* 1987, *65*, 626–629.

(9) It was found that use of less sterically hindered, more nucleophilic, strong bases, such as the hydroxide ion, led to decomposition of benzoylacetylene accompanied by production of a deep red color; the nature of this reaction was not investigated.

0022-3263/91/1956-4808$02.50/0 © 1991 American Chemical Society