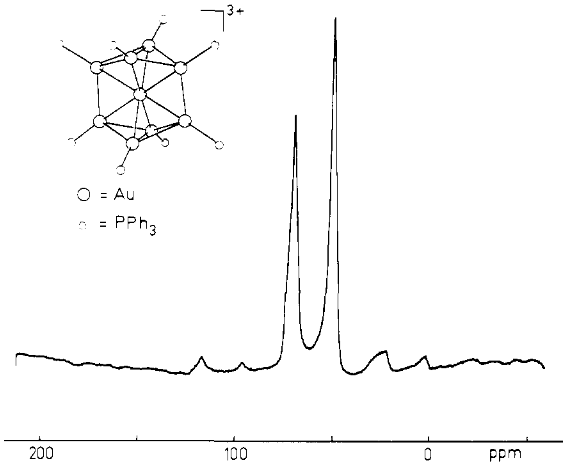

Figure 4. ^{31}P NMR spectrum of $[Au_9(PPh_3)_8][NO_3]_3$ (CP time 5 ms, pulse interval 5 s, 4710 accumulations, spinning rate 3.5 kHz).

ciation reactions.[9c] The only well-studied compound is $[\{(MeO)_3P\}_4Cu]^+$.[9a,b,d]

The Cu atom in $(Ph_3P)_2CuNO_3$ is tetrahedrally coordinated to the two phosphorus atoms and two oxygen atoms of the NO_3^- group.[10] The two triphenylphosphine groups are equivalent. The solid-state ^{31}P NMR spectrum of $(Ph_3P)_2CuNO_3$, Figure 2, shows four main peaks at +26.0, +13.1, -7.0, and -31.1 ppm, the outer peaks accompanied by satellite peaks at +28.3 and -33.1 ppm. The ^{65}Cu isotope (abundance ^{63}Cu 69.09%, ^{65}Cu 30.91%) seems to be responsible for these satellite peaks.

Because the crystal structure[10] shows that all phosphine groups are equivalent, the splitting of the phosphorus resonance line into four peaks has to be caused by coupling of the phosphorus spin ($I = {}^1/_2$) to the Cu spin ($I = {}^3/_2$ for both isotopes). Surprisingly, the splitting between the lines of this quartet increases to higher field. An explanation of this effect may be that due to the presence of a Cu quadrupole interaction not small compared to the Cu Zeeman interaction, the Cu-P dipolar and **J** tensor interactions are not averaged out by magic angle spinning. Then, in addition to the isotropic J coupling, also the dipolar and **J** tensor interactions contribute to the splitting. Analogous effects for $^{13}C-^{14}N$ couplings have been reported by Lippmaa and co-workers.[11] However, in their case also a broadening of the ^{13}C lines is found, while the ^{31}P lines of Figure 2 are only 2-ppm wide. In the absence of the Cu quadrupole interaction and without magic angle spinning, the Cu-P dipolar interaction would result in a more than 3-kHz-wide powder pattern, assuming the Cu-P distance to be 2.3 Å.[12] In this communication no attempt will be made to explain the unequal splittings together with the absence of severe line broadening. Both theoretical and further experimental work is under way to clarify this point.

In another copper complex, $(Ph_3P)_3CuCl$, the situtation is different. Here the crystal structure of $(Ph_3P)_3CuCl$ indicates that there are three molecules per unit cell, two are crystallographically identical, the third molecule being different.[13] The solid-state ^{31}P NMR spectrum of $(Ph_3P)_3CuCl$, Figure 3, shows resonances from the two different molecular sites at +9.9, -2.4, -15.3, and -27.9 ppm and at +7.6, -4.7, -17.2, and -29.9 ppm. Also ^{65}Cu satellite peaks appear on the outer signals. Here the splittings within one quartet are not very different, between 900 and 940 Hz. This indicates a smaller Cu quadrupole interaction as compared to $(Ph_3P)_2CuNO_3$, which is reasonable in view of the higher local symmetry (C_{3v}) around Cu in $(Ph_3P)_3CuCl$.

Of the few known gold cluster compounds the spectrum of one of the more interesting clusters, $[Au_9(PPh_3)_8][NO_3]_3$, is given in Figure 4. The spectrum shows two lines, the low-field one asymmetric, at +48.0 and +68.7 ppm.

Because the splitting is too large for a dipolar splitting (for a Au-P distance of 2.3 Å[12] the rigid lattice dipolar line width is calculated to be only 200 Hz), these lines must result from two inequivalent P sites, either in one molecule or in two, crystallographically inequivalent, molecules of the unit cell.

Unfortunately, the crystal structure is not known and no choice between these two possibilities can be made. In solution all phosphine groups are equivalent: in CD_2Cl_2 one sharp resonance is found at +57.1 ppm.[12]

We have now investigated 30 metal-phosphine complexes by high-resolution solid-state ^{31}P NMR. In this preliminary report only four representative spectra are shown, but it seems clear that NMR studies with solid-state line-narrowing techniques can provide valuable information about the structure of such complexes in powders.

Acknowledgment. This work was carried out partly under the auspices of The Netherlands Foundation of Chemical Research (SON) and with the aid of The Netherlands Organization for the Advancement in Pure Research (ZWO). We thank the Department of Inorganic Chemistry for providing us with the samples. Stimulating discussions with Dr. H. L. M. van Gaal are gratefully acknowledged. We thank Professors J. J. Steggerda and E. de Boer for their interest in this work.

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Received June 11, 1980

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(9) (a) R. W. King, T. J. Hutteman, and J. G. Verkade, *Chem. Commun.*, 561 (1965); (b) K. J. Coskram, R. D. Bertrand, and J. G. Verkade, *J. Am. Chem. Soc.*, **89**, 4535 (1967); (c) E. L. Muetterties and C. W. Alegranti, *ibid.*, **92**, 4114 (1970); (d) W. MacFarlane and D. S. Rycroft, *J. Magn. Reson.*, **24**, 95 (1976).

(10) G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, **8**, 2750 (1969).

(11) (a) E. Lippmaa, M. Alla, H. Raude, R. Teeäär, I. Heinmaa, and E. Kundla, Proceedings of the XXth Congress Ampere, Tallinn, 1978, E. Kundla, E. Lippmaa, and T. Saluvere, Eds., Springer Verlag, Berlin, Heidelberg, New York, 1979, p 87. (b) E. Kundla and M. Alla, *ibid.*, p 92.

(12) F. A. Vollenbroek, Thesis, Nijmegen, 1979. F. A. Vollenbroek, J. P. van den Berg, J. W. A. van der Velden, and J. J. Bour, *Inorg. Chem.*, **19**, 2685 (1980). Data are corrected with respect to 85% H_3PO_4.

(13) J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, O. A. Ucko, D. J. Barton, D. Stowens, and S. J. Lippard, *Inorg. Chem.*, **15**, 1155 (1976).

Deactivation of the Fluorescent State of 9-*tert*-Butylanthracene. 9-*tert*-Butyl-9,10-(Dewar anthracene)

Sir:

The fluorescence quantum yields of 9-alkyl-substituted anthracenes in solution at room temperature slightly increase from 0.29 for methyl to 0.39 for isobutyl.[1] Surprisingly, 9-*tert*-butylanthracene in *n*-heptane shows at room temperature a fluorescence quantum yield of only 0.011.[2] Besides the typical temperature dependence of the fluorescence quantum yield of meso-substituted anthracenes[3] in solution, 9-*tert*-butylanthracene exhibits a dramatic viscosity dependence of its fluorescence quantum yield. At room temperature the fluorescence quantum yield in glycerol increases to 0.10 and in the matrix of poly(methyl methacrylate) (PMMA) even to 0.43. Since, contrary to most of the meso-substituted anthracenes, we do not observe any triplet-triplet absorption within the resolution time of our microsecond flash photolysis apparatus, the strong decrease of the fluorescence in solution must be accompanied by a concomitant increase in radiationless deactivation of the fluorescent state of 9-*tert*-butylanthracene. Consequently, this can be an increased internal conversion by the *tert*-butyl group,[4] operating as a "loose

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(1) A. S. Cherkasov, *Bull. Acad. Sci. USSR, Phys. Ser.*, **20**, 436 (1956).

(2) S. Schoof, H. Güsten, and C. von Sonntag, *Ber. Bunsenges. Phys. Chem.*, **82**, 1068 (1978).

(3) S. Schoof, H. Güsten, and C. von Sonntag, *Ber. Bunsenges. Phys. Chem.*, **81**, 305 (1977).

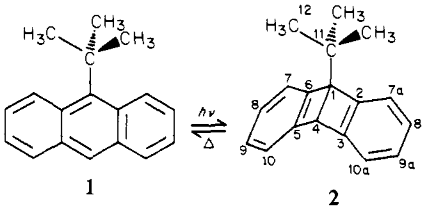
0002-7863/80/1502-7936$01.00/0

bolt",[5] and/or an unknown photochemical reaction.[6]

Irradition[7] of 2 L of a 3 × 10^{-4} M solution of 9-*tert*-butylanthracene (**1**), mp 105 °C, in isopentane at 0 °C results in a steady decrease of the ^1L_a absorption band at 371 nm down to complete disappearance. The remaining white crystals, mp 71–72 °C, exhibit the following spectroscopic properties: UV λ_{max} (*n*-hexane) 278 (ϵ 3070), 272 (ϵ 2810), 263 (ϵ 2230), 249 nm (ϵ 2140) [similar to hemi(Dewar naphthalene[8]) and benzocyclobutene[9]]; MS (70 eV) m/z 234 (40%), 219 (100%), 204 (34%), 191 (20%), 178 (44%) (same fragment ions and same metastable ions as 9-*tert*-butylanthracene;[10] however, their relative intensities differ enough to confirm the presence of an isomeric photoproduct in the ionization chamber of the mass spectrometer); PE(HeI) 7.40 and 7.60, 8.52, 9.16, 10.25, 11.10 E_i/eV with further superposition of the higher ionizations of 9-*tert*-butylanthracene;[11] ^{13}C NMR ($CDCl_3$; at −10 °C with off-resonance decoupling) δ 149.4 (s, C-2, C-6), 147.2 (s, C-3, C-5), 126.7 (d, C-8, C-8a), 126.5 (d, C-9, C-9a), 123.2 (d, C-7, C-7a), 123.0 (d, C-10, C-10a), 74.6 (s, C-1), 52.1 (d, C-4), 32.4 (s, C-11), 27.1 (q, C-12) [in good agreement with those of partly related systems such as [4.2.2]propella-7,9-diene,[12] benzobicyclo[2.2.1]heptadiene,[13] biphenylene,[14] *tert*-butyl-1,3,5-cycloheptatriene,[15] 1-methylnorbornene,[16] and dihydrohexamethyl(Dewar benzene)];[17] ^{1}H NMR (CCl_4, internal Me_4Si; at room temperature) δ 7.00 (8 H, m), 4.68 (1 H, s), 1.10 (9 H, s) [in good agreement especially for the bridgehead proton of hemi(Dewar naphthalene)].[8] No peaks attributable to 9-*tert*-butylanthracene were detected in freshly prepared solutions in the NMR spectra; however, a shoulder at 259 nm in the UV spectrum indicates the presence of 1.8% of 9-*tert*-butylanthracene. When the irradiation is performed in the absence of oxygen, the ^{1}H NMR spectrum exhibits two additional peaks (1.60 and 5.80 ppm in $CDCl_3$) which we tentatively assign to the *tert*-butyl groups and the bridgehead protons of the photodimer of 9-*tert*-butylanthracene (yield under 10%).

The spectroscopic data and especially the proton and ^{13}C NMR spectra are consistent with the structure of 1-*tert*-butyldibenzo-2,5-bicyclo[2.2.0]hexadiene [9-*tert*-butyl-9,10-(Dewar anthracene) (**2**)].

In solution, compound **2** thermally rearranges to **1**. The aromatization in *n*-hexane was followed at four temperatures over the range 29.6–61.4 °C by monitoring the increase of the 371-nm absorption of **1**. Kinetic analysis for the first-order reaction yielded the Arrhenius equation



1 2

$$\log k = (10.7 \pm 0.2) - (20500 \pm 500)/2.303RT$$

The activation energy E_a and the preexponential factor A are in reasonable agreement with the kinetic data for the aromatization of hemi(Dewar naphthalene) (E_a = 23.68 kcal/mol, log A = 12.30 s^{-1})[18] and 1,2,3,4-tetrachloro-9,10-(Dewar anthracene) (E_a = 24.47 kcal/mol, log A = 13.99 s^{-1}).[19] The activation enthalpy $\Delta H^{\ddagger}$ = 19.9 kcal/mol and the entropy $\Delta S^{\ddagger}$ = −11.0 ± 1 eu should be compared with those for the aromatization of monochloro(Dewar benzene) ($\Delta H^{\ddagger}$ = 19.1 kcal/mol, $\Delta S^{\ddagger}$ = −9.4 eu), Dewar benzene ($\Delta H^{\ddagger}$ = 23.0 kcal/mol, $\Delta S^{\ddagger}$ = −5.0 eu),[20] hemi(Dewar naphthalene) ($\Delta H^{\ddagger}$ = 23.02 kcal/mol, $\Delta S^{\ddagger}$ = −4.44 eu),[18] and 1,2,3,4-tetrachloro-9,10-(Dewar anthracene) ($\Delta H^{\ddagger}$ = 23.8 kcal/mol).[19] They indicate a substantial steric effect of the *tert*-butyl group. Obviously, among the alkyl groups the *tert*-butyl group strongly enhances the rate of the thermal rearomatization.[21]

The quantum yield[22] for the formation of **2** in *n*-heptane is only 0.012 and in glycerol, 0.01. Even in the rigid matrix of PMMA the photochemical valence isomerization **1** → **2** and the thermal rearomatization **2** → **1** can often be repeated. Contrary to the fluorescence the concomitant photochemical valence isomerization from the S_1 state depends only little on the viscosity of the solution. Thus, it appears that the rigid environment of glycerol and PMMA prevents the free rotation of the *tert*-butyl group. If we accept that the quantum efficiency for the intersystem crossing in **1** does not change when going from the solution to the rigid matrix, the *tert*-butyl group serves here as an efficient "loose bolt" to accelerate internal conversion in the solution,[4,5] which is the predominant radiationless decay process of the excited singlet state of **1** at room temperature. It is interesting that the *tert*-butyl group in aromatic molecules promotes internal conversion as well as photochemical valence isomerization, especially the production of Dewar isomers.[23-25]

Despite the low quantum yield of the photoreaction **1** → **2**, 9-*tert*-butylanthracene offers a promising potential for the conversion and storage of solar energy. Photochemical valence isomerization provides inherent advantages over other types of photochemical reactions because the energy storage capability is substantially larger. The exothermicity of Dewar systems is about 60 kcal/mol.[18,26,27] Unlike many other Dewar compounds,[23] **2** is photochemically accessible and **1** absorbs light from 410 to 300 nm with a high molar extinction coefficient (ϵ_{371} = 6.6 × 10^3 L mol^{-1} cm^{-1} in cyclohexane). The thermal half-life at 20 °C is 6.5 h, allowing a nearly 100% conversion of **1** into **2** with tropospheric solar light.

Acknowledgment. This work was performed on the basis of a German–Yugoslav scientific cooperation program. The financial support by the Internationales Büro, Kernforschungsanlage Jülich, and by the Republic Council for Science of Croatia (SIZ II) is gratefully acknowledged.

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Received April 30, 1980

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(4) W. W. Schloman, Jr., and H. Morrison, *J. Am. Chem. Soc.*, **99**, 3342 (1977).

(5) N. J. Turro, "Modern Molecular Photochemistry", Benjamin-Cummings, Menlo Park, Calif., 1978, p 170.

(6) H. Dreeskamp and J. Pabst, reported at the 6th GDCh meeting "Photochemie", Göttingen, Nov. 21–23, 1979.

(7) A water-cooled Pyrex immersion well with a 125-W Philips lamp was used as the light source.

(8) R. N. McDonald and D. G. Frickey, *J. Am. Chem. Soc.*, **90**, 5315 (1968).

(9) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

(10) L. Klasinc, S. Komadinović, D. Stefanović, and H. Güsten, *Croat. Chem. Acta.*, **48**, 109 (1976).

(11) L. Klasinc, B. Kovač, S. Schoof, and H. Güsten, *Croat. Chem. Acta*, **51**, 307 (1978).

(12) K. Weinges and K. Klessing, *Chem. Ber.*, **107**, 1915 (1974).

(13) K. Tori, T. Tsushima, H. Tanida, K. Kushida, and S. Satoh, *Org. Magn. Reson.* **6**, 324 (1974).

(14) H. Straub, *Justus Liebigs Ann. Chem.*, 1675 (1978).

(15) H. Günther and T. Keller, *Chem. Ber.*, **103**, 3231 (1970).

(16) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 7107 (1970).

(17) J. A. Turner and W. Herz, *J. Org. Chem.*, **42**, 1657 (1977).

(18) W. Grimme and U. Heinze, *Chem. Ber.*, **111**, 2563 (1978).

(19) W. Pritschins and W. Grimme, *Tetrahedron Lett.*, 4545 (1979).

(20) R. Breslow, J. Napierski, and A. H. Schmidt, *J. Am. Chem. Soc.*, **94**, 5906 (1972).

(21) J. E. Anderson and R. W. Franck, *J. Nouv. Chim.*, **3**, 717 (1979).

(22) The quantum yield was determined with potassium ferrioxalate actinometer.

(23) E. E. van Tamelen, *Acc. Chem. Res.*, **5**, 186 (1972).

(24) R. W. Franck, W. L. Mandella, and K. J. Falci, *J. Org. Chem.*, **40**, 327 (1975).

(25) D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **32**, 1309 (1976).

(26) J. F. Oth, *Recl. Trav. Chim. Pays-Bas*, **87**, 1185 (1968).

(27) W. Adam and J. C. Chang, *Int. J. Chem. Kinet.*, **1**, 487 (1969).

(28) Visting scientist from the University of Zagreb, Faculty of Technology, Department of Organic Chemistry.