Diphenyl Carbene Cation: Electronic and Molecular Structure

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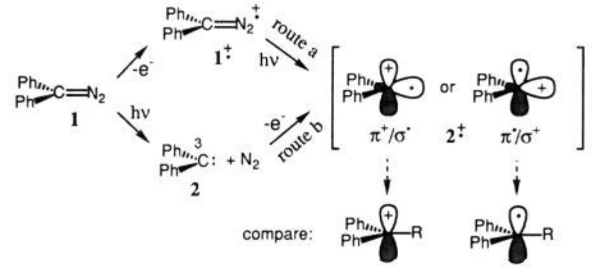
Carbene radical ions have been postulated repeatedly as intermediates in the (electro)chemical reduction or oxidation of diazo compounds and other precursors. Bethell and Parker have shown that unimolecular loss of N_2 from ionized diazo compounds does not represent a major reaction pathway in solution except in special cases,[2] i.e., the radical cations of diarylcarbenes which are formed upon electrochemical oxidation of the corresponding diazo precursors.[3] Such carbene species exhibit both electrophilic and radical-like reactivities, as expected for radical cations, but the kinetic experiments do not reveal whether the diaryl carbene cations (e.g., **2**$^{\bullet+}$) are $\sigma^+/\pi^\bullet$ or $\sigma^\bullet/\pi^+$ species (Scheme I).

Scheme I



In 1987, a Japanese group reported the preparation of phenyl- and diphenyldiazomethane radical cations in butyl chloride and $CFCl_3$ glasses and their subsequent photolysis.[4] The authors interpreted their optical and ESR spectra to indicate that the primary diazo radical cations lose N_2 upon visible irradiation and, hence, yield the corresponding carbene radical cations. However, the spectra did not contain enough information to allow for discussion of the electronic structure of the carbene radical cations.

Recent high-level *ab initio* calculations have confirmed that the ground state of parent $CH_2^{\bullet+}$ is $^2A_1$ (i.e., $\sigma^\bullet/\pi^+$ in our present terminology), the $^2B_1$ ($\sigma^+/\pi^\bullet$) state lying some 19.5 kcal/mol higher at the equilibrium geometry.[5] It is, however, not clear *a priori* whether the same state ordering remains preserved in (potentially nonplanar) phenyl-substituted derivatives. Therefore, this question was approached by preparing different isotopically substituted carbene cations with radiolytic oxidation in freon and argon matrices.[6] The experimental protocol involves formation of the carbene cation via two independent routes, i.e., (a) photolysis of the ionized diazo precursor and/or (b) ionization of photochemically preformed triplet carbene (cf. Scheme I). As **2** does not persist in halocarbon solvents, the latter route can only be followed in noble gas matrices. The corresponding results will be reported in a full paper,[7] while this communication focuses on the diphenyl derivative **2**$^{\bullet+}$ in freon glasses.

Thus, ionization of the diazo precursor **1** in a freon mixture[8] yielded a deep blue sample exhibiting spectrum 1a (Figure 1), which is attributed to **1**$^{\bullet+}$, in agreement with Kato et al.[4,9] Subsequent photolysis through a 540-nm cutoff filter yielded spectrum 1b, which we ascribe to **2**$^{\bullet+}$.[7] It was anticipated that the electronic structure of **2**$^{\bullet+}$ would reveal itself through the optical spectrum, because if the ground state was $\sigma^+/\pi^\bullet$, the optical spectrum should be comparable to that of $Ph_2C^\bullet H$ (λ_{max} = 330 nm[10]), while in the other case it should look more like that of Ph_2C^+H (λ_{max} = 440 nm[11]). As λ_{max} = 380 nm of **2**$^{\bullet+}$ falls right between the two above values, the question of whether diaryl carbene cations are σ or π radicals could not be answered on the basis of the optical spectra.

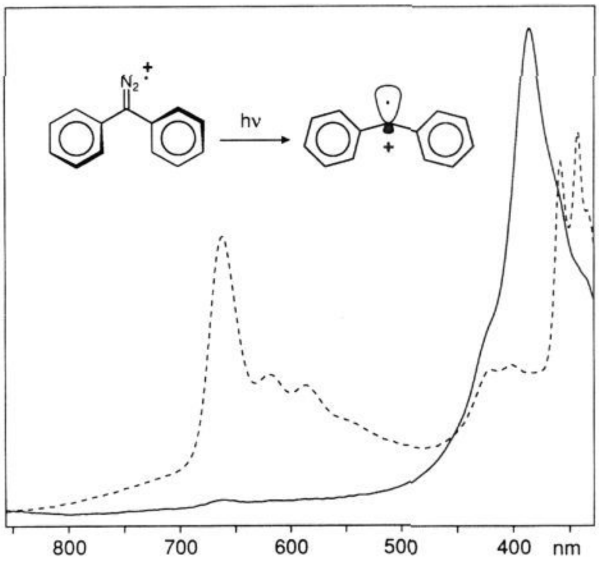


Figure 1. Spectrum obtained after ionization of **1** (a, dashed line) in a freon mixture[8] and after subsequent photolysis at $\lambda > 540$ nm (b, solid line). A spectrum nearly identical to b is obtained after ionization of photochemically preformed **2** in argon.[7]

Consequently, we resorted to ESR spectroscopy, whereby a curious problem was encountered: unlike Kato et al.,[4] we found that **1**$^{\bullet+}$ formed by radiolytic oxidation in $CFCl_3$ (or, in fact, in any of the other freons used currently for ESR spectroscopy of radical cations) is entirely photostable and lacks the intense blue color associated with the 650-nm band of **1**$^{\bullet+}$ observed in the optical spectra.[12] On the other hand, γ-irradiation of **1** in CF_2BrCF_2Br[14] gives rise to a blue sample showing an ESR spectrum similar to that previously reported for **1**$^{\bullet+}$ in $CFCl_3$.[4,12] It consists

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[1] Current address: Hoffmann-La Roche AG, Basel, Switzerland.

[2] Bethell, D.; Parker, V. D., *Acc. Chem. Res.* **1988**, *21*, 400.

[3] Parker, V. D.; Bethell, D. *J. Am. Chem. Soc.* **1987**, *109*, 5066.

[4] Kato, N.; Myiazaki, T.; Fueki, K.; Kobayashi, N.; Ishiguro, K.; Sawaki, Y. *J. Chem. Soc., Perkin Trans. II* **1987**, 881.

[5] Reuter, W.; Peyerimhoff, S. D. *Chem. Phys.* **1992**, *160*, 11.

[6] Bally, T. In *Radical Ionic Systems, Properties in Condensed Phase*; Lund, A., Shiotani, M., Eds.; Kluwer Academic Publishers: Dordrecht, 1991.

[7] Bally, T.; Matzinger, S.; Truttmann, L.; Platz, M. S.; Gerson, F.; Arnold, A.; Schmidlin, R., manuscript in preparation.

[8] A 1:1 mixture of $CFCl_3$ and CF_2BrCF_2Br (cf. Sandorfy, C. *Can. J. Spectrosc.* **1965**, *10*, 85. Grimison, A.; Simpson, G. A. *J. Phys. Chem.* **1968**, *72*, 1776). This mixture gives very clear glasses but melts at ≈80 K.

[9] The electronic structure of **1**$^{\bullet+}$ and **2**$^{\bullet+}$ will be discussed in the full paper.[7]

[10] Bromberg, A.; Meisel, D. *J. Phys. Chem.* **1985**, *89*, 2507.

[11] Olah, G. A.; Pittman, C. U.; Waack, R.; Doran, M. *J. Am. Chem. Soc.* **1966**, *88*, 1488.

[12] For **1**$^{\bullet+}$ in a $CFCl_3$ matrix we observed a different ESR spectrum than that observed by Kato et al.[4] It shows distinct additional features on both sides of the central absorption which are compatible with the solution spectrum of **1**$^{\bullet+}$ reported by Ishiguro et al. and interpreted in terms of a bent σ-radical cation.[13] We have currently no explanation for this difference from the experiments of Kato et al.,[4] but the intriguing possibility of a state crossover in **1**$^{\bullet+}$ induced by a change of solvent[14] is under investigation.

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mainly of a strong signal with a half-width of ca. 2 mT. Upon photolysis at $\lambda > 540$ nm, some weak features separated by ca. 8 mT, which must be due to $\mathbf{2}^{\bullet+}$, appear readily on both sides of this signal.

Use of **1** labeled with ^{13}C in the diazo carbon atom leads to a broadening of the ESR signal of $\mathbf{1}^{\bullet+}$, indicating an additional hyperfine interaction. Photolysis of $[^{13}C]\mathbf{1}^{\bullet+}$ has an impressive effect, as several strong anisotropic features are now observed which flank the signal of the precursor cation. At low temperatures (77–120 K), these features extend over a range of 30 mT and their interpretation is difficult. However, on raising the temperature to 140 K, an interesting transformation takes place which presumably arises from relaxation of the incipient $\mathbf{2}^{\bullet+}$.[15] The ESR spectrum collapses into a pattern which is readily analyzed in terms of parallel and perpendicular components $|A_{\parallel}| = 14.30 \pm 0.05$ and $|A_{\perp}| = 7.60 \pm 0.10$ mT for the ^{13}C coupling constant (Figure 2).

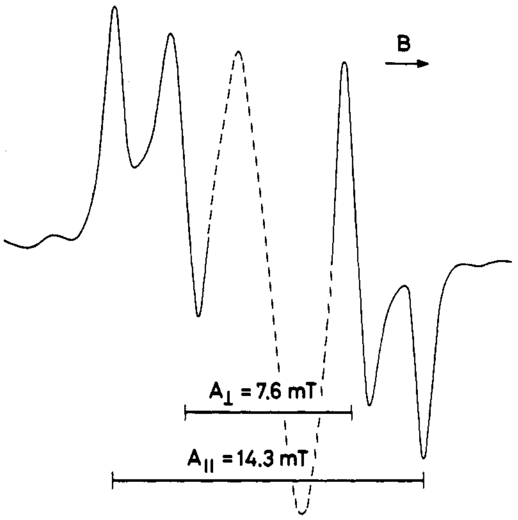

Figure 2. ESR spectrum of $[^{13}C]\mathbf{2}^{\bullet+}$ in CF_2BrCF_2Br at 140 K; g(almost isotropic) = 2.0027 ± 0.0003. The dashed part of the curve represents the signal due to unreacted $[^{13}C]\mathbf{1}^{\bullet+}$; its intensity decreases upon prolonged photolysis.

The corresponding isotropic constant $a_{iso} = {}^1/_3(A_{\parallel}+2A_{\perp})$ and the anisotropic contribution $B = {}^1/_3(A_{\parallel}-A_{\perp})$ have realistic values only if the sign of both $A_{\parallel}$ and $A_{\perp}$ is assumed to be positive. From $a_{iso} = (+)9.83 \pm 0.08$ and $B = (+)2.23 \pm 0.05$ mT thus obtained, one derives the spin populations $\rho(2s) = a_{iso}/A_0 = 0.073$ and $\rho(2p) = B/B_0 = 0.582$ by making use of the atomic parameters $A_0 = 134.7$ and $B_0 = 3.83$ mT.[16] While 9.83 mT greatly exceeds the ^{13}C-coupling constants (2.4–2.6 mT)[17a] found for the central C atom in derivatives of $Ph_2C^{\bullet}H$ as reference π radicals, it approaches the values (10–14 mT)[17b] observed for ^{13}C nuclei in paramagnetic centers of neutral σ-radicals of the acyl, vinyl, and phenyl types. Therefore, it is reasonable to classify $\mathbf{2}^{\bullet+}$ as a σ-radical with $0.073 + 0.582 = 0.655$ or $^2/_3$ of the total spin population localized on the central carbon atom.

In order to complement the above results, a set of *ab initio* calculations with the 3-21G basis set was carried out. In accord with qualitative expectations, these calculations showed the $\sigma^{\bullet}/\pi^{+}$ state to be substantially more stable than the $\sigma^{+}/\pi^{\bullet}$ state (55 kcal/mol at the ground-state equilibrium geometry). Geometry optimization of the $\sigma^{\bullet}/\pi^{+}$ state leads to a minimum with C_2 symmetry at $\alpha = 145°$ and $\epsilon = 15°$ (Figure 3).[18] An INDO calculation at this geometry yields an isotropic ^{13}C-coupling constant of 8.85 mT, in very good agreement with the value derived from the ESR spectrum. Furthermore, the energy of the $\sigma^{\bullet}/\pi^{+}$ state for different values of α shows that, similarly to parent $CH_2^{\bullet+}$,[5] the bending potential of $\mathbf{2}^{\bullet+}$ is very shallow. At the 3-21G equilibrium value of $\alpha = 125.3°$ for $\mathbf{1}^{\bullet+}$, the energy of $\mathbf{2}^{\bullet+}$ (optimized otherwise within C_2 symmetry) is only 5.9 kcal/mol higher than at $\alpha_{eq} = 145°$. This suggests that at 77 K the rigid matrix could well prevent the incipient $\mathbf{2}^{\bullet+}$ from relaxing completely to its (planar[18]) equilibrium structure, which can, however, be attained upon softening of the matrix, thus accounting for the changes observed between 77 and 150 K in the ESR spectra.[15]

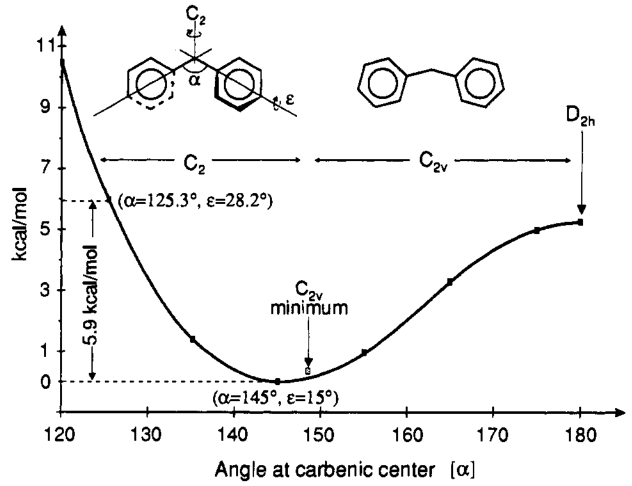

Figure 3. ROHF/3-21G potential energy surface for $\mathbf{2}^{\bullet+}$ from eight points fully optimized within C_2 symmetry (energies relative to the C_2 minimum, the total energy of which is −495.037 026 a.u.). Beyond 149°, structures assume C_{2v} symmetry (D_{2h} at 180°). The point at $\alpha = 125.3°$ corresponds to the equilibrium structure of the Ph_2C moiety in $\mathbf{1}^{\bullet+}$ calculated at the same level.

In conclusion, it has been shown that the ground state of diphenylcarbene radical cations is of $\sigma^{\bullet}/\pi^{+}$ nature, in agreement with qualitative expectations and with *ab initio* calculations which predict the $\sigma^{+}/\pi^{\bullet}$ state to lie significantly higher in energy. ESR spectra indicate that $\mathbf{2}^{\bullet+}$, which is initially formed in a twisted conformation similar to that of the precursor ion, only relaxes to its equilibrium structure after annealing of the matrix. Further work to elucidate the nature of the incipient $\mathbf{2}^{\bullet+}$ species observed at 77 K, as well as the identity of $\mathbf{1}^{\bullet+}$ formed in the bromide-free freons,[12] is in progress.

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(13) (a) Ishiguro, K.; Sawaki, Y.; Izuoka, A.; Suguwara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2530. (b) Ishiguro, K.; Ikeda, M.; Sawaki, Y. *Chem. Lett.* **1991**, 511.

(14) After some trials we found that the nature of the ionized **1** undergoes a dramatic change upon admixture of CF_2BrCF_2Br to $CFCl_3$ and that the characteristic blue color of $\mathbf{1}^{\bullet+}$ can only be observed when the matrix contains more than ≈20% of the bromide. Unfortunately, the above freon mixture[8] is ill suited for ESR experiments, but—somewhat unexpectedly—reasonably well-resolved ESR spectra could be obtained in *pure* CF_2BrCF_2Br, which has the additional advantage over its mixture with $CFCl_3$[8] that it can be warmed to nearly 150 K without inducing charge recombination. On the other hand, pure CF_2BrCF_2Br forms polycrystalline matrices, and it was, therefore, impossible to follow the changes of this matrix by optical spectroscopy in the UV upon annealing (where $\mathbf{2}^{\bullet+}$ has its main absorption).

(15) A similar relaxation upon softening of the matrix was invoked for neutral carbenes on the basis of ESR (Gilbert, B. C.; Griller, D.; Nazran, A. S. *J. Org. Chem.* **1985**, *50*, 4738) and, more recently, emission spectra (Despres, A.; Lejeune, V.; Migirdicyan, E.; Admasu, A.; Platz, M. S.; Berthier, J.; Flament, J. P.; Parisel, O.; Baraldi, I.; Momicchioli, S., manuscript in preparation.

(16) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

(17) Landolt-Börnstein, In *Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K. M., Eds.; Springer-Verlag: Berlin; 1977. (a) Vol. 9b, Chapter 4.7.2. (b) Vol. 17b, Chapter 3.2.

(18) Single-point calculations including correlation indicate that a planar (C_{2v}) equilibrium structure with a slightly larger angle α may actually be more stable. However, the hyperfine coupling constants are not strongly affected by this small geometry change. The result of full geometry optimizations at this level of theory will be reported in a full paper.[7]