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[9] A correct description of biradical intermediates needs a multireference configuration interaction (MR-CI) approach. However, because the biradical nature of the wavefunction develops after the transition state—that is, in the density functional theory (DFT) calculations $<S^2> = 0$ was found for all transition states (B. Engels, M. Hanrath, *J. Am. Chem. Soc.*, in press)—the influence of substituents on the activation energy of both processes can be obtained from less demanding DFT calculations. Consequently, in the present work the influence of the substituents at the alkyne terminus on the activation energy of both cyclizations was studied with the density functional approach in combination with a 6-31G* AO basis set, while an individually selecting MR-CI approach in combination with a DZP basis set (T. H. Dunning Jr., *J. Chem. Phys.* **1970**, *53*, 2823) was used for the computation of the reaction energies ($\Delta E_r$). The reference space of the individually selecting MR-CI computations consisted of up to 15 configurations, leading to total MR-CI configuration spaces of more than $500 \times 10^6$ configuration state functions (CSFs). The secular equations actually solved were in the order of $4 \times 10^6$ CSFs. The influence of the neglected CSFs was estimated by the Buenker–Peyerimhoff extrapolation (R. J. Buenker, S. D. Peyerimhoff, *Theor. Chim. Acta* **1975**, *39*, 217; R. J. Buenker, S. D. Peyerimhoff, W. Butscher, *Mol. Phys.* **1978**, *35*, 771; R. J. Buenker, R. A. Phillips, *J. Mol. Struct. THEOCHEM* **1985**, *123*, 291, and references therein). The influence of higher excitations are estimated by the normalized form of the Davidson correction (J. E. Del Bene, E. A. Stahlberg, I. Shaviatt, *Int. J. Quantum. Chem. Symp.* **1990**, *24*, 455). In these calculations, abbreviated in the following as MR-CI + Q, all valence electrons were correlated. The calculations were performed with the DIESEL-MR-CI program package (B. Engels, M. Hanrath, DIESEL-MR-CI (*d*irect *i*nternal *e*xternal separated individually *sel*ecting MR-CI) program package, Universität Bonn, Germany, **1997**; M. Hanrath, B. Engels, *Chem. Phys.* **1997**, *225*, 197). The transition states were optimized and characterized by frequency calculations. As discussed above, the DFT (B33LYP) approach was used (A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785). These calculations were performed with the Gaussian 94 program package (M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**) and the TurboMol program package (R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel, *Chem. Phys. Lett.* **1989**, *162*, 165; O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346).

[10] Experimental studies[7] provided an activation energy of 24–25 kcal mol$^{-1}$ for the $C^2$–$C^6$ cyclization for R = Ph, $R^1$ = *n*Bu, $R^2$ = $POPh_2$ (Scheme 1), while for R = H, $R^1$ = *n*Bu, $R^2$ = $POPh_2$ an activation energy of about 22 kcal mol$^{-1}$ was measured for the $C^2$–$C^7$ cyclization. Test calculations for R = H showed that the $POPh_2$ group lowers the barrier by about 3–4 kcal mol$^{-1}$.

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[13] Our calculations for R = H and R = Ph identify both biradical intermediates as minimum structures on the potential surface. A zwitterionic mechanism could be ruled out, because the first excited singlet state of the biradical intermediate, which has a zwitterionic structure, lies above the singlet ground state.

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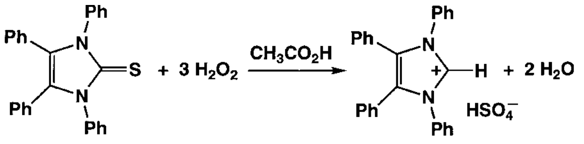
# 1,3,4,5-Tetraphenylimidazol-2-ylidene: The Realization of Wanzlick's Dream**

Anthony J. Arduengo III,* Jens R. Goerlich, Roland Krafczyk, and William J. Marshall

In 1970 H.-J. Schönherr and H.-W. Wanzlick postulated the formation of the title compound **3** upon deprotonation of the corresponding imidazolium perchlorate **2** · $ClO_4^-$ with potassium *tert*-butoxide.[1] However, carbene **3** was neither observed nor isolated, but rather allowed to react in situ with water in the presence of oxygen from the air. The resulting ketone, 1,3,4,5-tetraphenylimidazol-2-one, was characterized as the secondary reaction product. The apparent absence of any attempt to isolate the putative carbene **3** or its dimer may have been a result of the then prevalent idea that such imidazol-2-ylidenes really exist as the corresponding dimers (olefins)[2] or are at best highly labile intermediates.[3] Nonetheless, for steric and energetic reasons, Wanzlick postulated the presence of the carbene **3**.

We now report the synthesis, characterization, and X-ray crystallographic structure determination of **3.** A modification of the procedure published by Wanzlick makes it possible to isolate the carbene.[1] The imidazolium salt **2** · $HSO_4^-$ was obtained by oxidation of 1,3,4,5-tetraphenylimidazol-2-thione (**1**)[4] with a solution of 30% aqueous hydrogen peroxide in acetic acid [Eq. (1)].[1] The amount of hydrogen peroxide specified in Wanzlick's procedure for the preparation of this salt is insufficient to form the hydrogensulfate quantitatively. Three moles of hydrogen peroxide are required per mole of thione because sulfur remains in the product in the form of a hydrogensulfate counterion; it is not lost as sulfur dioxide as assumed by Wanzlick et al. Wanzlick and co-workers also reported conversion of the initially formed imidazolium salt into a perchlorate, which was in turn used in their attempts to generate the carbene. It is possible that traces of the hydrogensulfate anion (similar in size and molecular weight to perchlorate) contaminated their imidazolium perchlorate and



(1)

**1**

**2**•$HSO_4^-$

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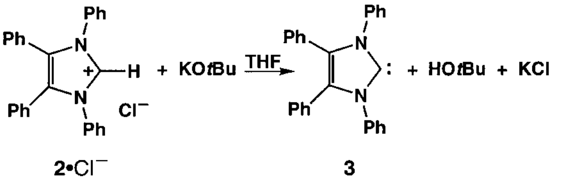
thus interfered with the deprotonation reaction because of the additional acidic proton. Our experience shows that imidazolium chlorides are more effective in subsequent deprotonation reactions than salts with other anions. Thus, the hydrogensulfate ion in $\mathbf{2}\cdot HSO_4^-$ was exchanged for chloride by treatment with barium chloride.

When $\mathbf{2}\cdot Cl^-$ is treated with potassium *tert*-butoxide in tetrahydrofuran (THF) at room temperature, the stable carbene **3** is formed through elimination of KCl and *tert*-butyl alcohol [Eq. (2)]. Carbene **3** is a colorless crystalline solid that melts at 199–202 °C with decomposition. Solid **3** tends to be microcrystalline and does not easily lend itself to satisfactory purification by recrystallization. This complication may be another reason why Wanzlick and co-workers did not report isolation of the carbene itself. However, we find that nice crystals of **3** can be grown by cooling solutions in THF/hexamethyldisiloxane.



(2)

The $^1H$ NMR spectrum of **3** shows a collection of multiplets at $\delta = 6.9-7.4$, but this provides little information about the compound. A signal at $\delta = 219.6$ in the $^{13}C$ NMR spectrum ([D$_8$]THF) of **3** clearly identifies the compound as a carbene and is very similar to resonances observed for other reported *N,N'*-diarylimidazol-2-ylidenes.[5, 6] The nitrogen centers in **3** produce a signal at $\delta = -161.2$ in the $^{14}N$ NMR spectrum, again providing data similar to that from previously reported *N*,N'-diarylimidazol-2-ylidenes.[5, 6]

Crystals suitable for X-ray diffraction studies were grown by cooling a solution of **3** in THF/hexamethyldisiloxane. The compound crystallizes in the orthorhombic space group $P2_12_12_1$.[7] Molecules of **3** are positioned such that a twofold symmetry axis passes through the carbene center and bisects the C4–C5 bond of the imidazole ring. Similar local symmetry is observed for 1,3,4,5-tetramethylimidazol-2-ylidene (**4**)[5] and 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene.[6] Selected bond lengths and angles for **3** and **4** as well as for 1,3-di-*p*-tolylimidazol-2-ylidene (**5**) are provided in Table 1. The crystalline structure of **3** is depicted as a KANVAS[8] drawing in Figure 1. The imidazole ring of **3** is nearly planar; only C4 and C5 lie respectively 0.5 pm above and below the average plane of the imidazole ring. The valence angle at the carbene center of **3** is 102.1°, which is characteristic of singlet carbenes.[5, 9] The nitrogen atoms are slightly pyramidalized; each lies 2.3 pm above the plane defined by its three attached substituents. The phenyl rings are twisted an average of 52° with respect to the imidazole plane and display a propellerlike geometry.

Table 1. Selected bond lengths [pm] and angles [°] for **3**–**5**.

| | 3 | 4 | 5 |
|---|---|---|---|
| *r*(C2-N1(3)) | 136.9(3) | 136.3(1) | 137.1(2), 137.5(2) |
| *r*(C4-C5) | 136.9(5) | 135.2(2) | 133.4(2) |
| *r*(N1(3)-C5(4)) | 140.9(3) | 139.4(1) | 139.2(2), 139.4(2) |
| *r*(N1(3)-Ph) | 144.0(3) | 145.4(1) | 143.0(2), 143.0(2) |
| *r*(C4(5)-Ph) | 147.7(3) | 149.0(1) | 95.6(16), 96.5(19) |
| *θ*(N1-C2-N3) | 102.1(3) | 101.5(1) | 101.2(1) |
| *θ*(C5(4)-N1(3)-C2) | 113.3(2) | 113.47(8) | 112.9(1), 113.0(1) |
| *θ*(N1(3)-C5(4)-C4(5)) | 105.7(1) | 105.78(5) | 106.6(2), 106.2(1) |
| *θ*(C2-N1(3)-Ph) | 119.5(2) | 122.9(1) | 123.1(1), 122.9(1) |
| *θ*(N1(3)-C5(4)-Ph) | 123.3(2) | 122.8(1) | 124(1), 123(1) |

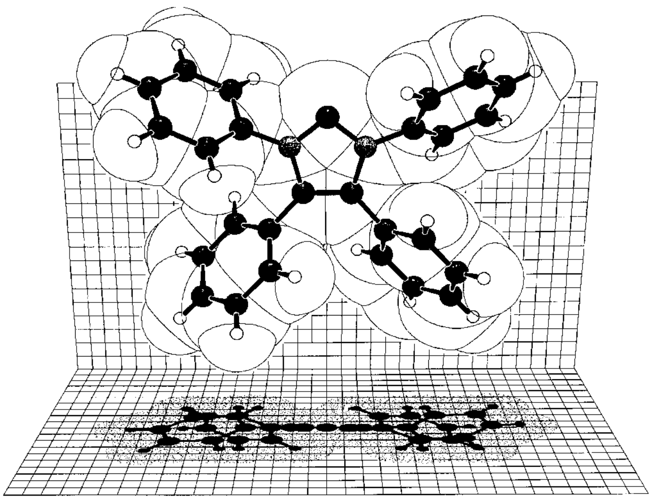


Figure 1. Space-filling KANVAS drawing of the crystalline structure of **3**.

The carbene **3** originally reported by Wanzlick and co-workers in 1970 does, in fact, exists as a monomeric carbene and not as a dimer. Furthermore, under the conditions described above it is possible to isolate **3** as a solid that is stable at room temperature in the absence of moisture and oxygen. The inconvenient physical properties of the carbene, possible problems with respect to purity of the starting material, and the then widely accepted idea that imidazol-2-ylidenes are too labile to be isolated in pure form probably all contributed to the fact that Wanzlick et al. did not actually isolate **3**.

## *Experimental Section*

$\mathbf{2}\cdot Cl^-$: To a solution of **1** (24.60 g, 60.81 mmol) in acetic acid (160 mL) was added dropwise at 100 °C of 30 % aqueous solution of $H_2O_2$ (22 mL, ca. 190.0 mmol). The resulting brown solution was heated under reflux for 1 h and subsequently allowed to cool to 23 °C. After 15 h the solvent was concentrated in vacuo to give a brown oil that contained $\mathbf{2}\cdot HSO_4^-$ together with traces of water and acetic acid. This crude product was dissolved in methanol (250 mL) and treated with a solution of $BaCl_2\cdot 2H_2O$ (14.85 g, 60.81 mmol) in water (50 mL). After removal of the $BaSO_4$ by filtration, the solution was concentrated in vacuo and the residue was triturated with ether (250 mL) to give crude $\mathbf{2}\cdot Cl^-$ as a beige solid. This was dried in vacuo and recrystallized from chloroform/toluene; yield: 16.2 g (65.1 %). M.p. 228 °C (decomp); $^1H$ NMR ($CDCl_3$): $\delta = 7.1-7.7$ (m, Ph), 10.1 (s, C2-H).

**3**: A 100-mL round-bottom flask was charged with $\mathbf{2}\cdot Cl^-$ (2.03 g, 4.96 mmol) and THF (20 mL). The resulting suspension was stirred for 15 min. Solid potassium *tert*-butoxide (0.59 g, 5.29 mmol) was added to the suspension at room temperature. A dark red solution was obtained immediately. The reaction mixture was stirred for 20 min, after which all volatiles were removed in vacuo. The residue was extracted into warm toluene (2 × 10 mL) and filtered through celite. The filtrate was concentrated and cooled to −25 °C, which caused **3** to crystallize; yield: 1.52 g (82.2 %). M.p. 199–202 °C (decomp); $^1H$ NMR ([D$_8$]THF): $\delta = 6.9-7.4$ (m, Ph); $^{13}C\{^1H\}$ NMR ([D$_8$]THF): $\delta = 127.121, 128.345$ ($C_{para}$), 127.256, 131.466

($C_{ortho}$), 128.871, 128.994 ($C_{meta}$), 131.197 ($C_{ipso}$ on C4,5), 131.894 (C4,5), 142.505 ($C_{ipso}$), 219.587 (C2); $^{14}$N NMR ([D$_8$]THF): $\delta = -161.21$ (s); EI-MS (70 eV): $m/z$ : 372.1600 [$M^+$], calcd for $C_{27}H_{20}N_2$: 372.1626.

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**Keywords:** carbenes · carbocations · imidazoles · imidazolylidenes

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[7] Crystal data for **3**: $T = -95\,^{\circ}$C, $\mathrm{Mo}_{K\alpha}$ radiation (Rigaku RU300 diffractometer, R-AXIS image plate area detector), crystal dimensions $0.18 \times 0.03 \times 0.25$ mm$^3$ (parallelepiped): $a = 1010.8(2)$, $b = 963.9(2)$, $c = 1035.2(2)$ pm, orthorhombic, space group $P2_12_12_1$ (no. 18), $Z = 2$, $\mu_{\mathrm{Mo}} = 0.67$ cm$^{-1}$, $M_r = 372.47$, $V = 1008.6$ Å$^3$, $\rho_{\mathrm{calcd}} = 1.226$ g cm$^{-3}$, filament size 12 × 2 mm, anode power 55 kV × 200 mA, crystal-to-plate distance 85.0 mm, 105-$\mu$ pixel raster, 45 frames, oscillation range 4.0° per frame, exposure time 25.0 min per frame, box sum integration, 5472 measured reflections, $4.0^{\circ} \leq 2\theta \leq 48.2^{\circ}$, max. $h,k,l = 11\,11\,11$, 1501 duplicates ($R_{\mathrm{merge}} = 0.023$), 772 independent reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least squares on $F$ (scattering factors from *Int. Tables for X-ray Crystallography, Vol. IV*). Carbon and nitrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions with isotropic temperature factors calculated as $1 + B_{\mathrm{iso}}$ of the corresponding carbon centers. The data/parameter ratio was 5.83. $R = 0.035$, $Rw = 0.032$, GOF = 1.43, $(\Delta/\sigma)_{\max} = 0.00$, max. residual electron density 0.12 e Å$^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101067. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] The drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL by E. Keller (Kristallographisches Institut der Universität Freiburg, Germany), which was modified by A. J. Arduengo III (E.I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.

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## Deposition of Data from X-Ray Structure Analyses

In order to make life easier for authors and referees the Cambridge Crystallographic Data Centre (CCDC) and the Fachinformationszentrum Karlsruhe (FIZ) have unified their procedures for the depostion of data from single-crystal X-ray structure analyses.

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