

- M. Wikstrom, K. D. Karlin, N. J. Blackburn, *ibid.* **1996**, *118*, 24–34; g) E. I. Solomon, U. M. Sundaram, T. E. Machonkin, *Chem. Rev.* **1996**, *96*, 2563–2605.
- [6] In the absence of azo derivatives **3** highly active benzylic alcohols undergo some aerobic oxidation to the corresponding aldehydes. For example, using 5 mol% CuCl·phen, 200 mol% K₂CO₃, benzene, 80 °C, and bubbling O₂ through the reaction mixture, a 60% conversion of *p*-chlorobenzylalcohol into *p*-chlorobenzaldehyde can be achieved. Allylic substrates gave much lower conversions (<30%) and aliphatic alcohols are virtually inert under these conditions. No reaction is observed with any of these substrates under anaerobic conditions, in the absence of the azo derivatives **3**.
- [7] The intermediacy of complex **7** in the aerobic oxidations was supported by the following observations: 1) independently generated hydrazido complex **7** (CuCl·phen/DBADH₂/NaH) proved to be unreactive under anaerobic conditions; 2) passing O₂ through the reaction mixture containing **7** and alcohol **2** restored the catalytic activity, and good yields of aldehyde **6** were again obtained.
- [8] This new catalytic cycle, involving steps **2** and **6**, is in some ways reminiscent of analogous oxidation shunts that take place in aerobic bacteria placed under anaerobic conditions.
- [9] The oxidation of alcohols with azodicarboxylates has been previously reported: F. Yoneda, K. Suzuki, Y. Nitta, *J. Org. Chem.* **1967**, *32*, 727–729. Control experiments were therefore performed to establish the need for copper salts in our anaerobic oxidation procedure. Thus, under our reaction conditions, no aldehyde or ketone could be detected in the absence of the CuCl·phen catalyst, even when phenanthroline was added as an activating base. Moreover, certain reactive alcohols were oxidized partially by CuCl·phen in the absence of the azo derivative **3**, though only in moderate yields.
- [10] With most oxidants, α -hydroxyketones are oxidized with concomitant cleavage of the C–C bond: a) R. C. Larock, *Comprehensive Organic Transformations*, VCH, New York, **1989**, pp. 604–615; b) R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**; c) G. Procter in *Comprehensive Organic Synthesis*, Vol. 7 (Eds.: B. M. Trost, I. Fleming, S. V. Ley), Pergamon, Oxford, **1991**; d) W. S. Trahanovsky, *Oxidation in Organic Chemistry, Part A–D*, Academic Press, New York.
- [11] See for example M. T. Reetz, M. W. Drewes, A. Schmitz, *Angew. Chem.* **1987**, *99*, 1186–1188; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1141–1143.
- [12] This difference appears to be due to competitive autooxidation of the aldehyde to the corresponding carboxylic acid by oxygen at high conversions of the alcohol. See also ref. [9b].

Electron-Density Relaxation and Oppositely Signed Reaction Constants in Dual Substituent Parameter Relationships in Dediazonation Reactions**

Rainer Glaser,* Christopher J. Horan, and Heinrich Zollinger*

Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

The reasons why relationship between σ and ρ in the Hammett equation [Eq. (1)]^[1] has been fairly well applicable since 1935 to several thousand heterolytic reactions of substituted benzene derivatives are by no means obvious. In the Hammett

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equation, the constants σ and ρ represent a combination of field (inductive) and resonance effects (mesomeric). One can therefore conclude that in all of these reactions both effects influence the reactivity in the same direction and to the same relative extent. This is indeed the case if one evaluates the same kinetic data with a dual substituent parameter (DSP) treatment, as, for example, developed by Taft and co-workers [Eq. (2)]; subscripts F and R indicate field and resonance effect contributions, respectively, to reaction rate constants k_X of X-substituted benzene derivatives relative to that of the unsubstituted compounds (k_0).^[2] Effects of electronic substituent can be classified^[3a] into those that are associated with the substituent's polarity (I_s , F , π_s , π_F) and those that are assigned to the substituent's ability to transfer charge (R , σ_n).^[3b] This classification relates the substituent constants σ_F and σ_R in Equation (2) to polarity and charge-transfer factors, as indicated in Equation (3).

$$\lg(k_X/k_0) = \sigma\rho \quad (1)$$

$$\lg(k_X/k_0) = \sigma_F\rho_F + \sigma_R\rho_R \quad (2)$$

$$\lg(k_X/k_0) = (\text{polarity})\rho_F + (\text{charge transfer})\rho_R \quad (3)$$

The substituent constants in the Hammett equation are assumed to be independent of the reaction.^[4] Dual substituent parameter treatments can thus be regarded as a necessary consequence of the two classes of intrinsic substituent effects. Experience shows that in the large majority of cases the ratio $\rho_R/\rho_F = \lambda \approx 1$. We estimate that values of λ larger than 1.1 or smaller than 0.9 (but still positive) are present in fewer than 10% of all equilibria and rates for which a Hammett relationship was tested. This result seems surprising, as the field and resonance effects are, in principle, considered to be independent of each other. There are, however, sixteen reactions with opposite signs for ρ_F and ρ_R , that is, λ is negative.^[5] Examples are dediazoniations of benzenediazonium ions in water, 1,2-dichloromethane, and trifluoroethanol; these reactions all show $\rho_F < -3.5$, $\rho_R > +2.2$, and $|\rho_F| > |\rho_R|$.

Due to our interest in the structure of benzenediazonium ions,^[6] the nature of C–N dative bonding,^[7] and its dediazoniations,^[5–8] we investigated the theoretical basis for the opposing influences of the field and resonance effects on dediazonation of *para*-substituted benzenediazonium ions *para*-X-C₆H₄-N₂⁺ (**1a**, X = H; **1b**, X = NH₂; **1c**, X = NO₂) to the respective *para*-substituted phenyl cations **2a–c** (see Figure 1). Zollinger interpreted the opposite signs of the reaction constants ρ_F and ρ_R by proposing that the cleavage of the σ bond between the N₂ lone pair and the sp² LUMO of **2** is slowed by inductively withdrawing substituents and should give rise to a substantial negative field reaction constant ρ_F . If N–C σ bonding is reinforced by C \rightarrow N π backbonding, a positive reaction constant ρ_R is plausible, since dissociation leads to an increase in π density on the phenyl fragment and brings π -electron density closer to the substituent. While this interpretation cannot be demonstrated experimentally, it is possible to examine it with electronic structure methods. We carried out electron-density analyses of the unimolecular dissociations **1** \rightarrow **2** + N₂ (X = H, NH₂, NO₂).

Our objectives here are to show that the reaction constants of the dediazonation reactions are consistent with the hypothesis of combined C \leftarrow N σ dative and C \rightarrow N π backdative bonding. Furthermore, we want to learn about the mechanisms by which two important substituents affect electronic structure. The electron-density analysis is based on the topological features of total electron densities, which are observable in the quantum me-

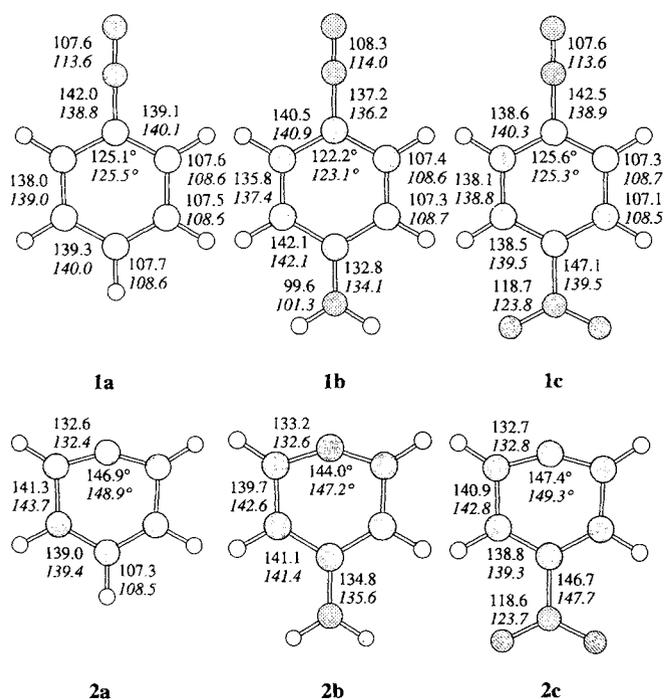


Figure 1. Structural parameters for **1a–c** and **2a–c** calculated at the levels RHF/6-31G* and MP2(full)/6-31G* (in italics). The *para* substituent is H, NH₂, and NO₂, respectively. The bond lengths are given in pm.

chanical sense. We also determined the σ and π components of the atom populations. Although these components are not observable, the concept of σ/π separation is successful and central to all models invoking dative and backdative bonding. In essence, our analysis links shifts in electron density in the σ and π systems with the reaction constants ρ_F and ρ_R . This approach differs slightly from Topsom's formulation,^[3] in which we would weigh π_σ and π_F with ρ_R . Ideally, an analysis of this relatively clear and qualitatively explainable case^[5] of a reaction with opposing field and resonance effects may lead to an understanding of why thousands of equilibria and reactions can be explained with the simple Hammett equation and show an almost constant ratio of the two effects ($1.1 > \lambda > 0.9$).

Structures along the dissociation pathways of **1a–c** were optimized at the RHF/6-31G* level,^[9, 10] and vibrational analyses were carried out for stationary structures. These dissociations proceed without an activation barrier, as in other diazonium ions.^[6, 7] Zero point energy corrections to binding energies were scaled by a factor of 0.9135.^[11] Geometries of stationary structures were refined at the MP2(full)/6-31G* level; the molecular models are shown in Figure 1. More reliable binding energies were computed at the levels up to QCISD(T,fc)/6-31G**/MP2(full)/6-31G* (Table 1).

Table 1. Binding energies and corrections of the vibrational zero point energy (VZPE) of **1** [a, b].

X	Reaction	RHF //RHF	Δ (VZPE)	MP2 //MP2	MP3(fc) //MP2	MP4(fc) //MP2	QCISD(T) //MP2
H	1a \rightarrow 2a + N ₂	107.22	-19.72	161.78	139.96	143.52	134.81
NH ₂	1b \rightarrow 2b' + N ₂	141.18	-19.05	199.75	178.02	177.86	165.67
NO ₂	1c \rightarrow 2c + N ₂	118.82	-19.30	180.12	154.87	160.73	150.93

[a] All values were calculated with the 6-31G* basis set. All energies are given in kJ mol⁻¹. [b] The Δ (VZPE) values need to be added to the reaction energies to obtain approximate reaction enthalpies: $\Delta H = \Delta E + \Delta$ (VZPE).

The C_{2v} structures **1a–c** are minima on the potential energy hypersurface, and **2a** and **2c** also prefer C_{2v} symmetry. However, a C_{2v} structure is not a minimum for **2b**. The most stable structure, labeled **2b'**, is nonplanar and chiral (C₁ symmetrical), and it appears advantageous for reducing ring strain at C_{ipso}. Structures **2b'** and **2b** are nearly isoenergetic, and the distortions do not play a role until late stages in the dissociation. Although we report binding energies for **2b'** in Table 1, we consider **2b** for the remaining discussion. The structural differences between **1a** and **1c** are minor (within 1 pm and 1°; Figure 1), while the effects of push–pull interaction are clearly manifest in **1b**. The structural relaxation upon N₂ dissociation is steady for all substituents X, and the major structural consequences are common. The main event concerns the rehybridization of C_{ipso} upon heterolysis: The C_{ipso}–C_{ortho} bond lengths shorten dramatically (by 0.06–0.08 pm), and the angle at C_{ipso} increases. Systematic studies of X/N₂⁺ systems showed that binding energies computed at the MP3 level or higher that include vibrational zero point energies reproduce experimental gas-phase binding energies nearly quantitatively.^[12] The good agreement between the data measured in the gas phase and in solution^[13, 14] suggests that primarily intrinsic properties of **1** are important in the solution chemistry. The binding energies of **1b** and **1c** are higher than for **1a**. The NH₂ and NO₂ groups are overall both electron-withdrawing groups, and are expected to destabilize the phenyl cation more than the diazonium ion. But why is the dissociation of **1b** more endothermic than that of **1c**? One might expect the opposite, since the nitro group is more electron-withdrawing, and because the π donor might better compensate for the electron deficiency in the σ framework. Therefore, qualitative considerations of **2** require significant differences in the electronic structures of **1b** and **1c** that provide an extra stabilization to **1b**. This realization leads to the idea of push–pull stabilization of spacer-connected π -donor–acceptor systems.

Topological electron density analyses^[15, 16] at the RHF/6-31G* level were carried out for stationary structures **1a–c** and **2a–c** and the associated reaction pathways; important results are shown in Figures 2 and 3. In general, aliphatic and aromatic diazonium ions are best thought of as carbenium ions closely associated with an N₂ molecule that is internally polarized in the fashion N $\alpha^{\delta-}$ –N $\beta^{\delta+}$. This bonding model implies C–N dative bonding instead of covalent C–N bond formation with charge transfer, as suggested by the formal Lewis notation. With a combination of theory and experiment, we have shown that the idea of a carbenium ion within the diazonium ion is fully warranted.^[17, 18] The integrated phenyl charge of **1a** is +0.974, and the N₂ group is nearly neutral and polarized (q (N α) = -0.540, q (N β) = +0.558). The charge distributions in the CN₂ regions of **1a** and **1c** are similar (Figure 2, top), and, as expected, **1c** exhibits a slightly higher positive N₂ charge.

In **1b** the charge q (H₂N–Ph) exceeds +1, and a negatively charged N₂ group occurs as the result of strong C \rightarrow N π backdonation of 0.338 electrons. This backdonation is about half as much in **1a** (0.211) and **1c** (0.185). For all ions **1**, the N \rightarrow C σ donation is the same, and the σ charge hardly varies from 0.231. The charge transfer associated with C–N bonding in **1** can thus be described by a bonding model that involves N \rightarrow C σ donation and C \rightarrow N π backdonation of about equal magnitudes (Scheme 1). The H_{para} atom in **1a** acts like the other aromatic H atoms to delocalize positive charge to the periphery of the molecule, while the X groups are negatively charged in **1b** and **1c**. The NH₂ group is a π donor (0.156 electrons), but overall it withdraws 0.475 electrons! The NO₂ group withdraws in total 0.531 electrons, of which 0.063 is due to π withdrawal.

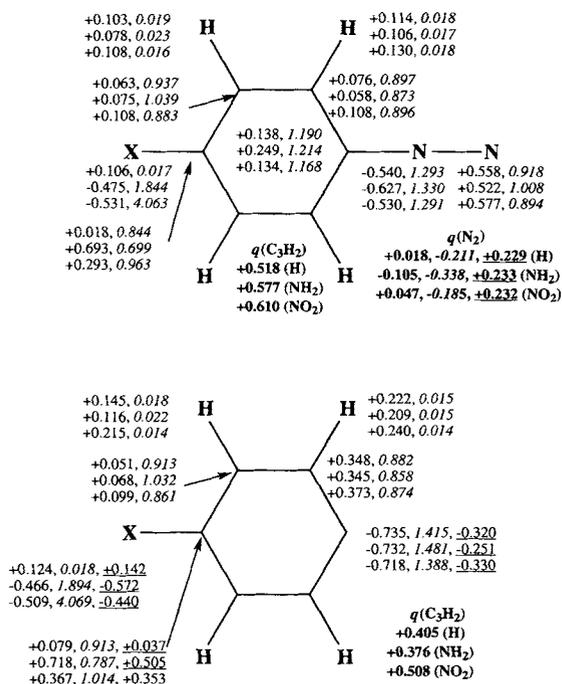
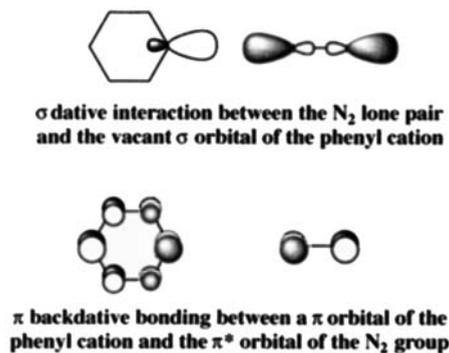


Figure 2. Integrated atom and fragment charges as well as populations (RHF/6-31G*) for **1a–c** and **2a–c**. The π populations are given in italics, and σ charges are underlined.



Scheme 1. Schematic representation of the primary MO interactions associated with $N \rightarrow C \sigma$ dative and $C \rightarrow N \pi$ backdative bonding in diazonium ions.

The density shifts show enhance $C \rightarrow N \pi$ backdative bonding in **1b**, but the electronic mechanism is more complex than the simplistic π -pushing picture and leaves the amino group very negative. The σ density of the N_2 group is changed slightly, but that of C_{ipso} is depleted; these events should strengthen $N \rightarrow C \sigma$ dative bonding in **1b**. Therefore, both components of the $C-N$ interaction are enhanced in **1b**. Compared to **1a**, the total changes in the charge of the N_2 group in **1c** are very similar to the changes in the π system. The NO_2 group leads to depletion of π density at C_{meta} , C_{ipso} , and N_β . These density shifts suggest that the NO_2 group hardly affects $N \rightarrow C \sigma$ dative bonding but weakens $C \rightarrow N \pi$ backdative bonding. The electron-density analysis suggests that $C-N$ bonding is enhanced in **1b** and weakened in **1c**; the $C-N$ bond lengths in **1a–c** are perfectly consistent with this trend.

Our analysis of the phenyl cations **2** focused on the C_3H_2 fragment and showed that its overall positive charge is greatly diminished during dediazonation: by 0.113 for $X = H$, by 0.102 for $X = NO_2$, and by as much as 0.201 for $X = NH_2$.

The σ -hole formation causes such extreme polarizations in the σ system that the majority of the positive charge is located on the other half of the molecule! Interestingly, the population analysis of **2** assigns a negative charge to C_{ipso} and large positive charges to the *ortho*-CH groups. These atom populations reflect $C_{ipso}-C_{ortho}$ bond polarization toward C_{ipso} and, with the zero-flux surfaces at a greater distance from C_{ipso} , an expanding C_{ipso} basin.^[7a, b] The topological analysis of the electronic relaxation along the dissociation path shows that the associated population changes at C_{ipso} reflect primarily inductomeric effects on the location of the $C_{ipso}-C_{ortho}$ partitioning surface.^[16]

The plots in Figure 3 depict the changes in $C-N$ bonding during heterolysis of **1a**; similar plots were obtained for the

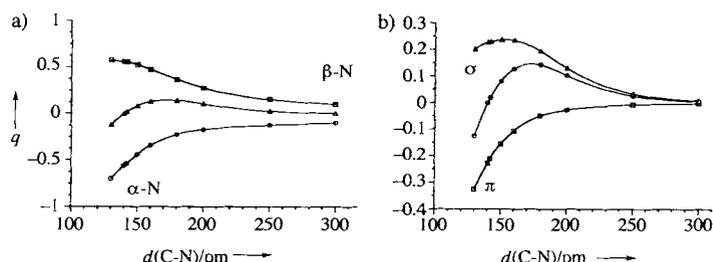


Figure 3. Variation of the charge q of a) the N atoms and b) the N_2 group as well as the σ and π components of the charge for **1a** along the unimolecular dissociation pathway as a function of the $C-N$ bond length. The top and bottom curves describe the different components, and the middle curve describes the corresponding combination.

substituted systems. The dissociation is essentially complete when the bond length $d(C-N)$ is about 300 pm. The charges of N_α and N_β change steadily, and the negative charge at N_α drops faster than the positive charge at N_β . Consequently, the charge of the N_2 group goes through a maximum around $d(C-N) = 175$ pm. Cleavage of the $C-N$ bond may increase ($X = H, NO_2$) or decrease ($X = NH_2$) the overall positive charge on the phenyl fragment. Irrespective of their charge in the equilibrium structures **1a–c**, the N_2 groups become more positive in the early phase of the dissociation, reach a maximum charge of 0.1–0.2 at $d(C-N) \approx 175$ pm, and then smoothly become neutral in the later stages. The value $q_{max}(N_2)$ for the NO_2 -substituted system exceeds that of the parent system; $q_{max}(N_2)$ of the NH_2 -substituted ion is the lowest. Our analysis illustrates in a compelling way that the $C \rightarrow N \pi$ backdative bond breaks earlier than the $N \rightarrow C \sigma$ dative bond.

These results are consistent with and provide additional support for the electron density based model that describes $C-N$ bonding in diazonium ions by synergistic $C \leftarrow N \sigma$ dative and $C \rightarrow N \pi$ backdative bonding. The analysis provides a straightforward theoretical basis for interpreting the oppositely signed DSP relationship and, in addition, furnishes details about the electronic structure that cannot be deduced from physical–organic studies alone. For example, the kinetic analysis does not answer the question as to whether the negative reaction constant ρ_F is due to positive charge being transferred from the diazo function onto the phenyl fragment (e. g. Lewis notation) or whether it is merely the result of charge shifts within the phenyl fragment (as we show). Only the theoretical analysis reveals how $C-N$ bonding is achieved. The kinetic analysis quantifies substituent effects on the overall energy difference between reagents and products, which form the basis for deducing stabilization mechanisms. Theory allows one to pinpoint

these mechanisms by providing independent information on both. While the overall charge of the phenyl fragments in **1** and **2** differ relatively little, the extreme polarizations in the σ systems of the phenyl cations cause a pronounced shift of positive charge from the C_3H_2 fragment into the other half of the molecule. We consider this electron density shift responsible for the negative reaction constant ρ_F . The phenyl ring gains π density upon dediazonation, which is consistent with the positive reaction constant ρ_R .

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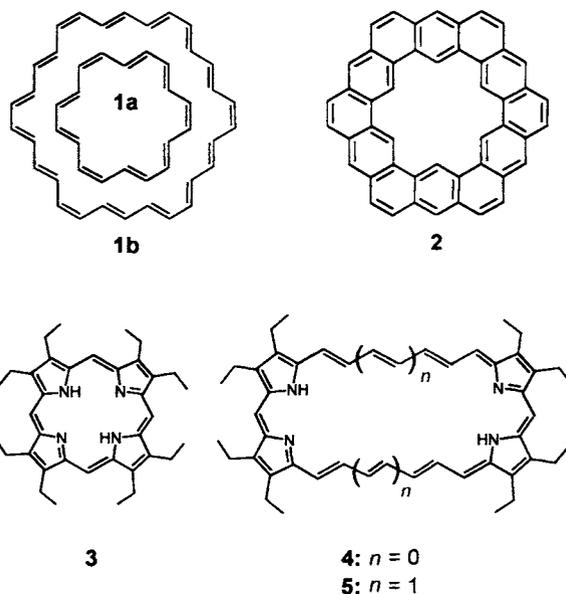
Keywords: bond theory · dediazonation · diazonium ions · electronic structure · linear free energy relation

- [1] L. P. Hammett, *Chem. Rev.* **1935**, *17*, 125.
 [2] a) R. W. Taft, *J. Am. Chem. Soc.* **1957**, *79*, 1045; b) S. Ehrenson, R. T. C. Brownlee, R. W. Taft, *Prog. Phys. Org. Chem.* **1973**, *10*, 1.
 [3] a) R. D. Topsom, *Prog. Phys. Org. Chem.* **1976**, *12*, 1; b) *ibid.* **1987**, *16*, 125.
 [4] a) E. R. Vorpapel, A. Streitwieser, S. D. Alexandratos, *J. Am. Chem. Soc.* **1981**, *103*, 3777; b) J. Niwa, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 226.
 [5] H. Zollinger, *J. Org. Chem.* **1990**, *55*, 3856.
 [6] a) R. Glaser, C. J. Horan, *J. Org. Chem.* **1995**, *60*, 7518, zit. Lit.; b) R. Glaser, M.-S. Son, *J. Am. Chem. Soc.* **1996**, *118*, 10942.
 [7] a) R. Glaser, G. S.-C. Choy, M. K. Hall, *J. Am. Chem. Soc.* **1991**, *113*, 1109; b) R. Glaser, G. S.-C. Choy, *ibid.* **1993**, *115*, 2340; c) R. Glaser, D. Farmer, *Chem. Eur. J.* **1997**, *3*, 1244.
 [8] H. Zollinger, *Diazo Chemistry I*, VCH, Weinheim, **1994**, chapters 8–10.
 [9] Gaussian94, revision C.3: 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, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, 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. J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1995**.
 [10] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.
 [11] J. A. Pople, A. P. Scott, M. W. Wong, L. Radom, *Isr. J. Chem.* **1993**, *33*, 345.
 [12] C. J. Horan, R. Glaser, *J. Phys. Chem.* **1994**, *98*, 3989.
 [13] a) T. Kuokkanen, P. O. I. Virtanen, *Acta Chem. Scand. Ser. B* **1979**, *33*, 725; b) T. Kuokkanen, *ibid.* **1990**, *44*, 394.
 [14] P. Burri, G. H. Wahl, H. Zollinger, *Helv. Chim. Acta* **1974**, *57*, 2099.
 [15] a) R. F. W. Bader, *Atoms in Molecules, A Quantum Theory*, Oxford University Press, New York, **1990**; b) F. W. Biegler-König, R. F. W. Bader, T.-H. Tang, *J. Comput. Chem.* **1982**, *3*, 317; c) R. F. W. Bader, P. L. A. Popelier, T. A. Keith, *Angew. Chem.* **1994**, *106*, 647; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 620.
 [16] Electron-density analyses were also carried out for **1a** and **2a** at the correlated levels MP2(full)/6-31G* (including dissociation pathways) and CISD(full)/6-31G*/RHF/6-31G*; similar results were obtained: R. Glaser et al., unpublished results.
 [17] a) R. Glaser, G. S. Chen, C. L. Barnes, *Angew. Chem.* **1992**, *104*, 749; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 740; b) G. S. Chen, R. Glaser, C. L. Barnes, *J. Chem. Soc. Chem. Commun.* **1993**, 1530.
 [18] R. Glaser, C. J. Horan, *Can. J. Chem.* **1996**, *74*, 1200, and references therein.

Hexavinyllogous Porphyrins with Aromatic 30 π -Electron Systems**

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The seminal work of Sondheimer et al. on the synthesis of cyclic conjugated compounds, including the aromatic [18]annulene (**1a**), culminated with the preparation of [30]annulene (**1b**).^[1] Although **1b** follows the $(4n+2)$ rule^[2] for aromatic systems, it is unstable. Perfect conformational stabilization of a C_{30} perimeter is achieved in kekulene **2** synthesized by Staab and Diederich.^[3] However, the π -electron sextets of its annelated benzene rings do not allow the formation of a conjugated 30 π perimeter. Recently it has been shown with numerous examples that planar cyclopolynes can be stabilized by insertion of pyrrole units,^[4–7] but no aromatic compound corresponding to [30]annulene (**1b**) has been synthesized so far.



After we had found that the *tetravinyllogous* porphyrin **4** has a stable aromatic 26 π -electron system,^[8] the question arose whether the stabilizing effect of the pyrrole units would be sufficient for a *hexavinyllogous* porphyrin **5**, which has a conjugated perimeter corresponding to the [30]annulene (**1b**) of Sondheimer et al.^[1] One serious impediment was that the synthesis of **5** would have to proceed via the highly reactive pyrrolypolyene **11** (Scheme 1).

We report here on the first synthesis of a hexavinyllogous porphyrin **5** with an aromatic 30 π -electron system. In addition to its importance for the understanding of aromaticity, this octaethyl[30]porphyrin is also of practical interest, as its parent compound, octaethyl[18]porphyrin **3**,^[9] is the most extensively used porphyrin in chemistry and medicine.

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