# Diheteroarylmethanes. 8.[1] Mapping Charge and Electron-Withdrawing Power of the 1,2,4-Triazol-5-yl Substituent

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Three new triazolyl derivatives, bis(1*H*-1-phenyl-1,2,4-triazol-5-yl)methane (**11**), 1*H*-1-phenyl-5-(*β*-styryl)-1,2,4-triazole (**12**), and 1*H*-5-benzyl-1-phenyl-1,2,4-triazole (**13**) have been synthesized and the carbanions **11**$^-$ and **13**$^-$ investigated in DMSO by multinuclear NMR spectroscopy. By applying previously proposed and widely used $\pi$-charge/$^{13}$C shift relationships on the spectra of the anions, it is possible to rank the $\pi$ electron-withdrawing power of the 1,2,4-triazol-5-yl group in terms of charge demand $c_X$, a quantity that represents the fraction of $\pi$ negative charge delocalized by the heterocyclic ring. Our results indicate that the charge demand $c_X$ of this heterocycle is considerably greater than that of other 1,3-azoles (2-imidazolyl, 2-oxazolyl, 2-benzoimidazolyl), being close to that of some mono- and diazinyl substituents. A single set of resonances is presented by both carbanions **11**$^-$ and **13**$^-$, thus showing that they exist either as a single geometric isomer species or as a mixture of isomers in a rapid (on the NMR time scale) equilibrium. $^{13}$C and $^{15}$N shift/$\pi$-charge relationships allow accurate $\pi$-charge mapping of carbanionic systems. Our results clearly show that, in the case of benzyl carbanion **13**$^-$, all of the three nitrogen atoms are almost equally involved in delocalizing the negative charge. Also, the *N*-phenyl group contributes to charge delocalization. Anion **11**$^-$ is the first of the bis(heteroaryl)methyl carbanions that we have studied, in which all of the negative charge originated by deprotonation of the carbon acid **11** is hosted on the nitrogen atoms without any appreciable involvement of the heteroaromatic carbon frame.

A number of the properties of heteroaromatic-based compounds ultimately depend on their geometric and electronic structure. Among other applications, the hot field of organic materials for nonlinear optics[2] has stressed the strict dependence of benchmark parameters (first and second hyperpolarizabilities) on the electronic nature of the constituting parts.[3] In particular, it has been shown that there is an optimal value of the electron-withdrawing and electron-donating strength of the end-cap substituents of push−pull conjugated systems, which leads to enhanced activities.[4] Fine-tuning of the design and synthesis strategy for achieving highly efficient heterocycle-based organic materials requires a knowledge of the extended quantitative scale of the electron-withdrawing capacity of as many heteroaromatic rings as possible.

Over the last 10 years, we have proposed $^{13}$C (relationships 1 and 2)[5,6] and $^{15}$N (relationship 3)[7−10] shift/$\pi$-charge relationships as a method of choice for experimentally mapping $\pi$-charges and ranking the resonance electron-withdrawing power of primary organic functionalities[6,11,12] and heterocycles, including azines (2- and 4-pyridyl, pyrazinyl, 4-pyrimidyl, 3-pyridazinyl, and 2- and 4-quinolyl),[7,11,13] 1,3-azoles (2-oxazolyl, 2-thiazolyl, 2-imidazolyl, and their benzo-fused analogues),[14] and purines (8-purinyl).[15]

(1) For part 7, see ref 15. For part 6, see ref 14b. For part 5, see ref 14a.

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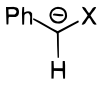
**Table 1. Charge Demand of Various Substituents (X) in Carbanions $1^-$ ($c_X^X$) and $2^-$ ($c_X^{Ph}$)[a]**

| X | $c_X^{Ph}$ | $c_X^X$ |
|---|---|---|
| Ph[b] | 0.29 | 0.29 |
| $CONMe_2$[b] | 0.42 | 0.275 |
| $CO_2Me$[b] | 0.40 | 0.268 |
| COMe[b] | 0.51 | 0.325 |
| COPh[b] | 0.56 | 0.341 |
| CN[b] | 0.28 | 0.207 |
| SOPh[b] | 0.26 | 0.233 |
| $SO_2Ph$[b] | 0.28 | 0.206 |
| $PO(OEt)_2$[b] | 0.26 | 0.122 |
| 2-thiazolyl[c] | 0.413−0.380 | 0.318 |
| 2-oxazolyl[c] | 0.346 | |
| *N*-methylimidazol-2-yl[c] | 0.283 | 0.254 |
| 2-benzothiazolyl[c] | 0.457−0.471 | 0.316 |
| 2-benzoxazolyl[c] | 0.424−0.436 | 0.288 |
| *N*-methylbenzimidazol-2-yl[c] | 0.382 | |
| 2-pyridyl[d,e] | 0.411 | 0.302 |
| 4-pyridyl[d,e] | 0.408 | 0.299 |
| 2-quinolyl[e] | | 0.313 |
| 3-pyridazinyl[f] | 0.417 | |
| 2-pyrimidyl[f] | 0.430 | |
| 4-pyrimidyl[f] | 0.501 | |
| pyrazinyl[f] | 0.446 | |
| *N*-methylpurin-8-yl[g] | 0.536 | 0.305 |

[a] The $c_X^X$ values are smaller than the $c_X^{Ph}$ values because of saturation phenomena; the two sets of values are linearly related (refs 8, 11, 12, and 16). [b] References 6 and 12. [c] Reference 14a. [d] Reference 11. [e] Reference 13b. [f] Reference 7. [g] Reference 15.

Relationship 1 allows empirical calculation of the $\pi$-electron density $q_C^\pi$ [5,6] on a trigonal carbanionic carbon (systems $\mathbf{1}^-$ or $\mathbf{2}^-$) when the chemical shift of the

$\mathbf{1}^-$



$\mathbf{2}^-$

carbanionic carbon and the NMR shielding contributions $A_i$ of the various substituents directly bonded to the anionic site are known.[5] Relationships 2 and 3 correlate the shift variation for each carbon or nitrogen site (which do not experience rehybridazation upon deprotonation) of $\mathbf{1}^-$ and $\mathbf{2}^-$ with that of the $\pi$-electron density going from the neutrals to the anions, thus providing empirical site-by-site charge mapping of the carbanions.

$$\delta^{13}C = 122.8 + \Sigma A_i - 160(q_C^\pi - 1) \quad (1)$$

$$\Delta\delta^{13}C = -160\Delta q_C^\pi \quad (2)$$

$$\Delta\delta^{15}N = -366.34\Delta q_N^\pi \quad (3)$$

We have defined the charge demand $c$ of a substituent group X as the fraction of $\pi$-charge transferred from a negatively charged trigonal carbon atom to the adjacent X group.[6,11,12] In particular, the symmetric carbanions $\mathbf{1}^-$ originate the $c_X^X$ values, whereas the benzyl carbanions $\mathbf{2}^-$ originate the $c_X^{Ph}$ values. The charge demands are directly related to $q_C^\pi$, the $\pi$-electron density on the (deprotonated) carbanionic carbon atom. Relationships 4 and 5 can be used to obtain the charge demand $c_X^X$ and $c_X^{Ph}$, respectively.

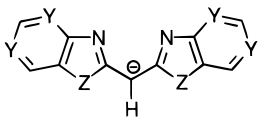
$$c_X^X = (2 - q_C^\pi)/2 \quad (4)$$

$$c_X^{Ph} = 2 - c_{Ph} - q_C^\pi \quad (5)$$

The $c_{Ph}$ value represents the charge delocalized onto the phenyl group in $\mathbf{2}^-$ and can be calculated according to relationship 6 (which is directly related to eq 2), by adding the local variations of the $\pi$-electron densities at all of the positions of the phenyl ring.

$$c_{Ph} = \Sigma\Delta q_{C-ring}^\pi = -\Sigma\Delta\delta^{13}C_{ring}/160 \quad (6)$$

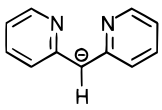
In this way, we obtained the two sets of $c_X^X$ and $c_X^{Ph}$ values listed in Table 1 for the various heterocyclic groups. The first set was obtained by applying multinuclear NMR spectroscopy to the investigation of type $\mathbf{1}^-$ diactivated systems (such as the symmetrically substituted carbanions $\mathbf{3}^-$, $\mathbf{4}^-$, $\mathbf{5}^-$, and $\mathbf{6}^-$ originated by deprotonation of bis(benzothiazol-2-yl)methane,[14a] bis(benzoxazol-2-yl)methane,[14a] bis(7-methylpurin-8-yl)methane,[15] and bis(pyrid-2-yl)methane[13b], respectively). The second set of values was similarly obtained considering type $\mathbf{2}^-$ α-benzyl anions, such as $\mathbf{7}^-$, $\mathbf{8}^-$, $\mathbf{9}^-$, and $\mathbf{10}^-$, which were obtained from the corresponding benzyl derivatives 2-benzylbenzothiazole,[14a] 2-benzylbenzoxazole,[14a] 8-benzyl-7-methylpurine,[15] and 4-benzylpyridine,[6,8,11,13a] respectively.



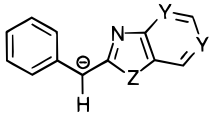
$\mathbf{3}^-$ : Z = S, Y = CH

$\mathbf{4}^-$ : Z = O, Y = CH

$\mathbf{5}^-$ : Z = NMe, Y = N



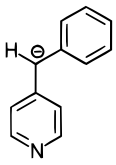
$\mathbf{6}^-$



$\mathbf{7}^-$ : Z = S, Y = CH

$\mathbf{8}^-$ : Z = O, Y = CH

$\mathbf{9}^-$ : Z = NMe, Y = N



$\mathbf{10}^-$

The ranking of electron-withdrawing capacities allows a precise prediction of the $^{13}C$ shift of the carbanionic carbon in many di- and trisubstituted carbanions.[8,9,16] It is also possible to describe the $\pi$-electron density variation associated with the deprotonation of the neutral to the conjugated anionic species and then obtain a charge map of the anion. In addition, we have shown that carbanions $\mathbf{2}^-$ can be present in DMSO as a mixture of both *E* and *Z* isomers because of the partial double bond between the carbanionic carbon and the $C_{ipso}$ of the heterocycle or the phenyl ring. The latter has been observed exclusively in the case of the anion of 2-benzyl-*N*-methylimidazole[14a] and has been rationalized in terms of charge demands. The charge demand of the 2-imidazolyl group is not only the smallest among the heterocycles we have considered but is also quite small in absolute terms. Consequently, whereas azines and other 1,3-azoles are good competitors of the phenyl ring in

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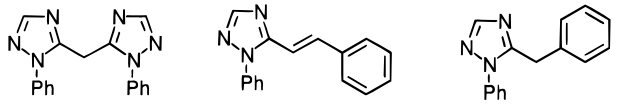
delocalizing the negative charge, imidazole is not, thus demonstrating that the hindered rotation occurs along different bonds in the two cases. We have recently reported[15] that the 8-purinyl substituent has the highest charge demand value of the heterocycles we have considered; in this case, the poor electron-withdrawing capacity of the imidazolyl ring was improved by an appropriate fusion with the pyrimidine system, the charge demand of which was determined to be very highly ranked.[7]

In this paper, we show how we increased the charge demand of the imidazolyl function by introducing a further azine-like nitrogen atom into the imidazole ring. We here report the synthesis of bis(1*H*-1-phenyl-1,2,4-triazol-5-yl)methane (**11**) and the results of the $^{13}$C NMR study of the corresponding sodium salt in DMSO, which was undertaken in order to determine the $c_X^X$ value. In analogy with our previous studies, we obtained the shielding contribution $A_i$ of the 1,2,4-triazol-5-yl substituent as the difference in the shifts of $\beta$-carbons in styrene and 1*H*-1-phenyl-5-($\beta$-styryl)-1,2,4-triazole (**12**). Finally, we synthesized 1*H*-5-benzyl-1-phenyl-1,2,4-triazole (**13**) in order to obtain the $c_X^{Ph}$ value from the $^{13}$C shifts of the corresponding carbanion.



**11** **12** **13**

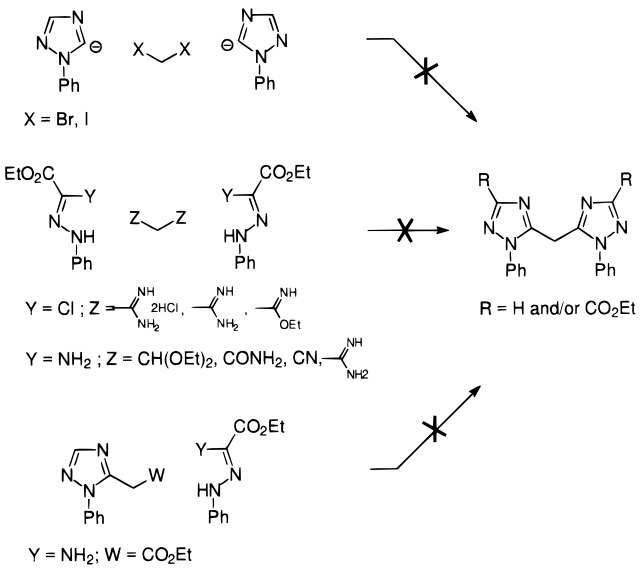
## Results

**Synthesis.** To the best of our knowledge, all of the compounds **11**−**13** were previously unknown in the literature. Although 5-substituted triazoles are prepared by means of well-known procedures starting from different precursors,[17] we found it difficult to apply one of them to the preparation of the bis-triazolylmethyl skeleton present in **11**. We attempted various synthetic approaches involving either preformed triazolyl rings (which we tried to link by inserting a methylene bridge) or open-chain systems suitable for ring closure to triazoles (Scheme 1).

Unfortunately, none of these reactions gave the target compound **11**, which was prepared in three steps following the procedure shown in Scheme 2. Ethyl α-amino-α-(phenylhydrazono)glyoxylate (**14**) reacted with malonyl chloride in toluene to give bis(1*H*-3-ethoxycarbonyl-1-phenyl-1,2,4-triazol-5-yl)methane (**15**) in very poor yield (4%). When acetonitrile was used under the same conditions, although still low, the yield increased to 8%. No alternative routes to **15** were successful in our hands. Subsequent acidic hydrolysis using 20% HCl gave biscarboxylic acid **16** in very good yields. Decarboxylation of **16** led to the symmetrically substituted methylene derivative **11** in lower yields than expected because, in addition to the desired product, bis-cyanoamide **17** was obtained (Scheme 3). The side product **17** was isolated and fully characterized.

The styryltriazole **12** was obtained according to Scheme 4. 1*H*-1-Phenyl-1,2,4-triazole (**18**) was lithiated at the five

**Scheme 1**




position using BuLi and reacted with MeI to give 1*H*-5-methyl-1-phenyl-1,2,4-triazole (**19**). Condensation of the latter with benzaldehyde in DMSO−NaOH afforded **12**.

Finally, the benzyl derivative **13** was prepared according to Scheme 5, following the same synthetic procedure as that used for **11**. The glyoxylate derivative **14** was reacted with phenylacetyl chloride in toluene to give the triazolylester **20**, which was hydrolyzed under acidic conditions to afford the corresponding acid **21**. Subsequent decarboxylation at 200 °C with Cu powder gave the pure benzyltriazole **13** in an 18% overall yield. No attempt was made to optimize this yield since the obtained amount was sufficient for our purposes.

**Preparation of Carbanions.** Carbanions **11**$^-$ and **13**$^-$ were prepared in DMSO using dimsylsodium as a base. We have previously documented elsewhere the reasons for our choice of DMSO as a solvent.[5−11] Given the well-known properties of DMSO as a highly dissociating medium and a good coordinating system for the sodium cation, the sodium salts of our carbanions should have the form of solvent-separated ion pairs or free ions. Under these conditions, the effect of the sodium gegenion on $\pi$-electron distribution in the anions should be minimized or much reduced in comparison with other common organic solvents. On the other hand, the many merits of DMSO are somewhat offset by the instability of its conjugate base above 60 °C, as well as by the fact that its high melting point prevents low-temperature NMR studies.

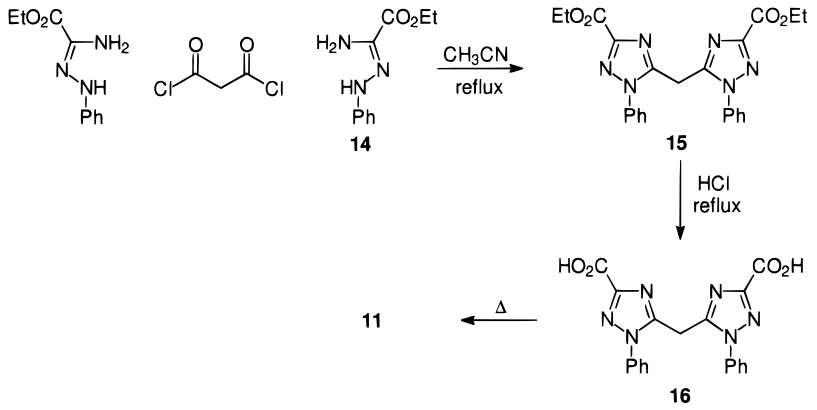
**NMR Shift Assignments.** The $^{13}$C and $^{15}$N shift assignments in the neutral compounds **11** and **13**, and their corresponding anions **11**$^-$ and **13**$^-$, are shown in Table 2. We here provide a detailed interpretation of the NMR data only in relation to those cases in which the assignment was not straightforward.

**(a) $^{13}$C Shifts.** 1*H*-1-Methyl-1,2,4-triazole was used as a model comparative compound.[18] The $^{13}$C shift assignments in the neutral compounds **11** and **13** were

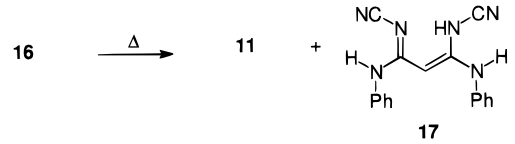
(17) Temple, C., Jr. Triazole 1,2,4. In *The Chemistry of Heterocyclic Compounds*; Montgomery, J. A., Ed.; Wiley: New York, 1981; Vol. 37.

(18) (a) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH: Weinheim, 1987; p 282. (b) Kalinowski, H. O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: Chichester, 1988; p 386.

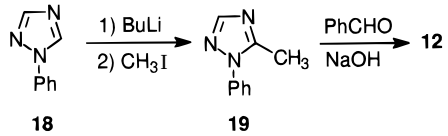
**Scheme 2**



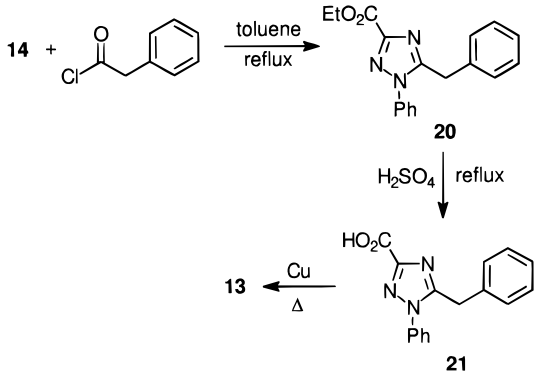
**Scheme 3**



**Scheme 4**



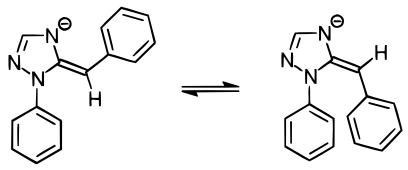
**Scheme 5**



based on coupling constants and the known heteroatom substituent effects operating in the heterocycle. In the case of ambiguity, the spectrum was analyzed completely and the discrimination based on the multiplicity of patterns and values of the long-range coupling constants. In compound **13**, the two ipso carbon atoms have a very similar chemical shift value, and their assignment may be exchanged. However, this uncertainty does not introduce any significant error in the evaluation of $c_X^{Ph}$.

**(b) $^{15}$N Shifts.** The results of our previous investigations of aza-heterocycle-based anionic systems[7,13,14a,15] have shown that both pyridine- and pyrrole-like nitrogen atoms undergo high-field displacement when passing from the neutrals to the anions because of the increase in the $\pi$-electron density on the nitrogen atoms in the anions. The shift assignments of these three nitrogen atoms of the triazole ring in compounds **11** and **13** were based on known nitrogen shielding in the unsubstituted 1*H*-1-methyl-1,2,4-triazole:[19] in anions **11**$^-$ and **13**$^-$, all of the nitrogen atoms are shielded with respect to their corresponding atoms in the neutrals. On the basis of this, it is assumed that the chemical shift order of the three nitrogen atoms of the neutrals is maintained in the anions. Consequently, the pyrrolic nitrogen atom remains at a higher field than the two pyridic nitrogen atoms.

**Geometric Isomerism in the Anions.** Unlike all of the benzylazoles we studied, the $^{13}$C NMR spectrum of the benzyl anion **13**$^-$ shows a single set of resonance in DMSO at 27 °C. This result indicates either the presence of a single species (*E* or *Z* geometric isomer) or a rapid (on the NMR time scale) equilibration between the interconverting isomers. The presence of geometric isomers is due to the partial $\pi$ character of the bond linking the carbanionic carbon and the $C_{ipso}$ of either the heterocycle or the phenyl group. The carbanion of 2-benzyl-*N*-methylimidazole was the only one showing hindered rotation along the bond linking the phenyl group at room temperature. We explained this result in light of the poor charge demand of the imidazolyl substituent in comparison with that of the phenyl group. In fact, the $^{13}$C spectra of all of the other studied benzylazoles and benzylazines (in which the heterocycle is a stronger electron-withdrawing group than the phenyl substituent) provided evidence of a mixture of both the *E* and *Z* isomers along the other bond. We believe that only the (*E*)-**13**$^-$ isomer



(*E*)-**13**$^-$ (*Z*)-**13**$^-$

was present in the present case for two reasons. First, the charge demand of the triazolyl substituent is greater than that of the benzoimidazolyl and close to those of the highly ranked 2- and 4-pyridyl and 2-thiazolyl; all of the corresponding benzyl anions exist as a mixture of the *E* and *Z* isomers. It is therefore likely that the bond between the carbanionic carbon and the heterocycle in **13**$^-$ has a double-bond character due to the electron-withdrawing property ($c_X^{Ph}$) of the triazolyl substituent. Second, the hypothetical planar (*Z*)-**13**$^-$ isomer would have a severe steric hindering effect on the two phenyl groups.

(19) Witanowski, M.; Stefaniak, L.; Webb, G. A. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1986; Vol. 18, p 445.

**Table 2. $^{13}C^{a}$ and $^{15}N^{b}$ NMR Shifts (ppm) of Bis(1*H*-1-phenyl-1,2,4-triazol-5-yl)methane (11), Its Conjugate Carbanion ($11^-$), 1*H*-5-Benzyl-1-phenyl-1,2,4-triazole (13), and Its Conjugate Carbanion ($13^-$) in DMSO[c]**

| | triazole ring positions | | | | | *N*-phenyl ring positions | | | | phenyl ring positions | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | N(1) | N(2) | C(3) | N(4) | C(5) | ortho | meta | para | ipso | ortho | meta | para | ipso | $CH_2/CH^-$ | $^1J$, Hz[d] |
| **11** | 221.2 | 298.9 | 151.13 | 254.3 | 150.79 | 124.70 | 129.47 | 129.06 | 136.65 | | | | | 24.64 | 132.8 |
| **$11^-$**[e] | 187.9 | 272.6 | 150.69 | 209.4 | 156.66 | 123.38 | 129.26 | 125.38 | 140.70 | | | | | 51.19 | 154.3 |
| **13** | 220.3 | 298.9 | 151.04 | 254.5 | 154.09 | 124.99 | 129.47 | 128.99 | 137.03[f] | 128.46 | 128.41 | 126.61 | 136.17[f] | 31.74 | 130.0 |
| **$13^-$**[e] | 182.8 | 265.7 | 150.40 | 212.7 | 156.21 | 121.43 | 128.65 | 122.31 | 142.30 | 119.99 | 127.43 | 111.44 | 145.21 | 65.29 | 150.1 |

[a] Relative to $Me_4Si$ (0.0 ppm). [b] Relative to liquid $NH_3$ (0.0 ppm), 380.23 from neat nitromethane. [c] 0.50 M solutions at 27 °C, unless otherwise noted. [d] Relative to the methylene or methine bridge. [e] 0.10 M. [f] Values can be exchanged.

**Table 3. Variations of the Local $\pi$-Electron Densities $\Delta q^{\pi}$ (millielectrons) for Each *i*th Position on Going from the Neutral Bis(1*H*-1-phenyl-1,2,4-triazol-5-yl)methane (11) and 1*H*-5-Benzyl-1-phenyl-1,2,4-triazole (13) to Their Conjugate Anions $11^-$ and $13^-$, Respectively[a,b]**

| | triazole ring positions | | | | | *N*-phenyl ring positions | | | | phenyl ring positions | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | N(1) | N(2) | C(3) | N(4) | C(5) | ortho | meta | para | ipso | ortho | meta | para | ipso |
| **$11^-$** | 91 | 72 | 3 | 122 | −37 | 8 | 1 | 23 | −25 | | | | |
| **$13^-$** | 102 | 91 | 4 | 114 | −13 | 22 | 5 | 42 | −33 | 53 | 6 | 95 | −56 |

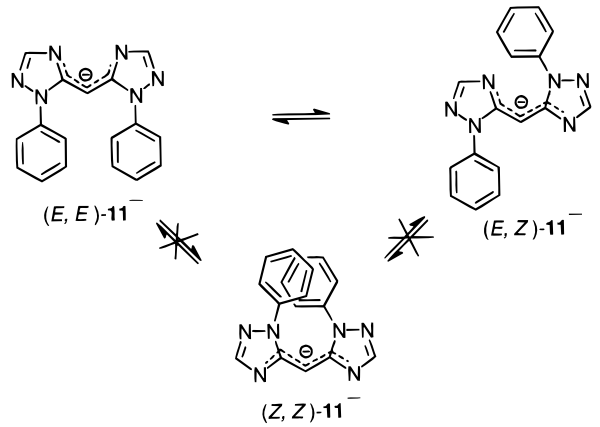
[a] Positive values correspond to an increment of $\pi$-electron density. [b] Obtained from $\Delta q^{\pi} = -(\Delta\delta^{13}C/160)$ and $\Delta q^{\pi} = -(\Delta\delta^{15}N/366.34)$ for carbon and nitrogen atoms.

Semiempirical calculations using the AM1 and the PM3 SCF-MO Hamiltonian included in the MOPAC package[20] were made for the two geometric isomers of anion **$13^-$**. The counterion was not included in the calculation in order to mimic the nature of anionic species in DMSO, in which they exist as solvent-separated or free ions. Both the AM1 and PM3 computations predicted that the *E* isomer should be the most stable (by 4.6 and 4.5 kcal/mol, respectively). Since the semiempirical approach is usually considered to be sufficiently accurate in terms of geometry optimization, the computed planar structure of the (*E*)-**$13^-$** isomer (against the nonplanarity of all of the three rings in the second isomer) suggests that its predicted higher stability is justified by its more efficient delocalization along the entire system.

Like the above benzyl carbanion, the $^{13}C$ NMR spectrum of the anion **$11^-$** shows a single set of resonances in DMSO at 27 °C. However, unlike the benzyl derivative **$13^-$**, two strong electron-withdrawing groups compete equally in delocalizing the negative charge of the adjacent carbanionic center. As a result, the bond between the carbanionic carbon and the heterocycle has a lower double-bond character, and thus a lower rotational barrier, than in **$13^-$**. It is therefore not possible to exclude either the hypothesis that one isomer predominates in the equilibrium (as in **$13^-$**) or that suggesting the existence of rapid interconversion involving a number of isomers [(*E*,*E*)-**$11^-$**, (*E*,*Z*)-**$11^-$**, and (*Z*,*Z*)-**$11^-$**].

However, it is reasonable to postulate that the inherent instability of the (*Z*,*Z*)-**$11^-$** isomer would prevent it from being significantly present in the equilibrium. This isomer clearly cannot exist as a planar system because of the presence of the bulky phenyl rings. Both the AM1 and the PM3 calculations in the gas phase indicated a pseudohelical structure in which none of the four rings are in the same plane. The computed energy of this system was found to be 5 kcal/mol larger than those of isomers (*E*,*E*)-**$11^-$** and (*E*,*Z*)-**$11^-$**, which fall within the 0.5 kcal/mol range.

(20) MOPAC 6.0: Stewart, J. J. P. *QCPE* 455, **1990**. All of the calculations were made using the keywords AM1 or PM3, EF, PRECISE, and CHARGE = −1. The geometries were fully optimized without any constraint, in the gas phase.




***π*-Charge Mapping of the Anions and Charge Demands of the 1*H*-1,2,4-Triazol-5-yl Substituent.** The variations in the local $\pi$-electron density of the trigonal carbon and nitrogen atoms going from the neutrals **11** and **13** to the conjugated anions **$11^-$** and **$13^-$** are shown in Table 3: these values can be calculated from relationships 2 and 3, respectively. The $\pi$-electron densities $q_C$ of the central carbanionic carbon obtained from relationship 1, and both of the aromatic rings, $q_{Het}$ and $q_{Ph}$, in **$11^-$** and **$13^-$**, are shown in Table 4. Once the $\pi$-electron densities of the fragments constituting **$11^-$** and **$13^-$** are known, the total $\pi$-electron density $q_{tot}$ can be calculated by means of relationships 7 and 8 (Table 4).

$$q_{tot} = q_C + 2q_{Het} \quad (7)$$

$$q_{tot} = q_C + q_{Het} + q_{Ph} \quad (8)$$

The excellent agreement of these empirically computed values with the theoretical number of $\pi$-electrons of systems **$11^-$** and **$13^-$** once again proves the highly reliable nature of our approach and validates the computed values given in Tables 3−5. Finally, Table 5 shows the charge demands $c_X^{Ph}$ and $c_X^X$ of the 1*H*-1-phenyl-1,2,4-triazol-5-yl ring, which were calculated by applying relationships 4 and 5 and using data from Table 4. Details of the procedure have been previously reported.[14]

## Discussion and Conclusion

In this study, we prepared a new and interesting series of 5-substituted triazoles **11**−**13** previously unknown in

**Table 4. Experimental $\pi$-Electron Densities *q* (electrons) for Conjugate Anions $11^-$ and $13^-$ of Bis(*1H*-1-phenyl-1,2,4-triazol-5-yl)methane (11) and *1H*-5-Benzyl-1-phenyl-1,2,4-triazole (13)**

| compd | $q_{Het}$[a] | $q_{Ph}$[b] | $q_C$[c] | $q_{tot}$[d] |
|---|---|---|---|---|
| $\mathbf{11}^-$ | 12.267 | | 1.429 | 25.96[e] |
| $\mathbf{13}^-$ | 12.361 | 6.157 | 1.432 | 19.95[f] |

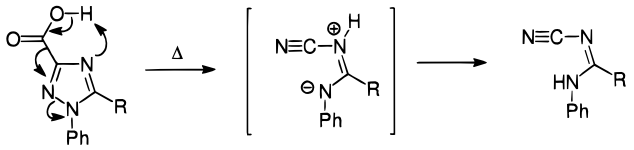
[a] $\pi$-Electron density resident on the triazole ring (including *N*-phenyl ring): $q_{Het} = 12 + \Sigma(\Delta q^{\pi})_{triazole\ ring}$; data are taken from Table 3. [b] $\pi$-Electron density resident on the phenyl ring linked to the carbanionic carbon: $q_{Ph} = 6 + \Sigma(\Delta q^{\pi})_{phenyl\ ring}$; data are taken from Table 3. [c] $\pi$-Electron density resident on the carbanionic carbon, calculated applying relationship 1, using $A_{Ph} = 13.00$ (ref 6), $A_{triazole} = -1.45$ (see Table 5) and chemical shift values reported in Table 2. [d] Total $\pi$-electron density of the anionic system, to be compared with the theoretical value of 26 and 20 $\pi$-electrons for $\mathbf{11}^-$ and $\mathbf{13}^-$, respectively. [e] Calculated according to relationship 7. [f] Calculated according to relationship 8.

**Table 5. Shielding Contribution $A_X$ and Charge Demand of the 1*H*-1-Phenyl-1,2,4-triazol-5-yl Substituent in Carbanions $13^-$ ($c_X^{Ph}$) and $11^-$ ($c_X^X$)**

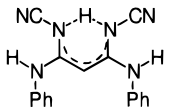
| $A_X$[a] | $c_X^{Ph}$ [b] | $c_X^X$ [c] |
|---|---|---|
| −1.45 | 0.411 | 0.286 |

[a] Calculated from the difference between the shifts of $\beta$-carbons in 1*H*-1-phenyl-5-($\beta$-stiryl)-1,2,4-triazole (**12**) (111.75 ppm) and styrene (113.2 ppm; ref 18b, p 161); see text. [b] Calculated applying relationship 5, with $c_{Ph} = q_{Ph} - 6$; data are taken from Table 4. [c] Calculated applying relationship 4; data are taken from Table 4.

**Scheme 6**



the literature. The styryl and benzyl derivatives **12** and **13** were obtained following classic organic syntheses of 5-substituted triazoles, but no efficient synthetic routes to the diactivated system **11** were found. It is worth noting that the final product yields were significantly different even though the same synthetic procedure was applied (the condensation of **14** with the appropriate acyl chloride, hydrolysis, and final decarboxylation).[21] Although alternative synthetic approaches to **11** were explored, they were unfortunately unsuccessful. The decarboxylation of the symmetrical bis-carboxyclic acid **16** unexpectedly occurred in much lower yields than that of the corresponding benzyl derivative **21**. The low yields were caused by the preferred competitive ring opening of the triazole rings of **16**. The ring opening in the pyrazole[22] and isoxazole[23] series to the corresponding cyano derivatives under basic conditions are known. It has also been reported[24] that 4-phenyl-1,2,4-triazole converts to phenylcyanamide when titrated with BuLi. Since the carboxylic acids of the 1,2,4-triazole series are known to be readily decarboxylated on heating but otherwise stable,[25] the behavior of the triazolyl ring in **16** seems to be unprecedented, although the cleavage of **16** can be interpreted on the basis of the reaction mechanism shown in Scheme 6, in which N(4) may act as a base promoting the reaction. This interpretation is supported by the experimental observation[23a] that 3-carboxypyrazoles decarboxylate without decomposition when heated at 250 °C; the presence of a base such as quinoline is necessary in order to observe ring opening. Since no products arising from ring opening were detected in the decarboxylation of monoacid **21**, we believe that the formation of the bis-cyanoamide **17** is particularly favored by the high degree of stability probably provided by the six-membered chelate arrangement **22**.



**22**

The use of our multinuclear NMR approach and charge demand values provide interesting insights into the electronic nature of the triazole system.[23] First, the existence of anion $\mathbf{13}^-$ as a single geometric isomer is the consequence of the steric hindrance between the two phenyl groups and the partial $\pi$-character of the bond linking the carbanionic carbon and C(5) of the triazolyl ring. Conversely, anion $\mathbf{11}^-$ may exist as a mixture of the *E,E* and *E,Z* isomers. In addition, the $c_X^{Ph}$ value (0.411) of this substituent is much higher than that of the imidazolyl moiety, the charge demand of which ranks low among the heterocycles so far investigated (Table 1). It is reasonable to imagine that this increase in the electron-withdrawing capacity of the triazolyl group is mainly caused by the introduction of the third nitrogen atom in the para position with respect to the carbanionic center, a position suitable for delocalizing the charge.

In benzyl anion $\mathbf{13}^-$, the three nitrogen atoms of the heterocyclic moiety are almost equally involved in the delocalization process, as each bears about 27% of the negative charge of the *N*-phenyltriazolyl group. This means that almost 80% of the delocalized negative charge is hosted on the nitrogen atoms, a value that becomes 100% in the case of the symmetrically disubstituted carbanion $\mathbf{11}^-$. This last represents the first case among the heterocycles we have studied in which all of the negative charge delocalized from the carbanionic center onto the heterocyclic ring is supported by the heteroatoms without any significant involvement of the aromatic carbon atoms. The lack of a negative $\pi$-charge resident on the carbon atoms of anion $\mathbf{11}^-$ is exactly the average result of increases and decreases in $\pi$-electron density in comparison with the neutral precursor. It is interesting to note that the phenyl ring bonded to N(1) of the heterocycle in benzyl anion $\mathbf{13}^-$ participates in delocalizing the negative charge even though no resonance structures can be written in which the negative charge moves from the carbanionic atom to the phenyl group: the $\pi$-electron density of the *N*-phenyl group increases by 63 millielectrons from **13** to $\mathbf{13}^-$ (Table 3), which represents about 20% of the $c_X^{Ph}$ of the *N*-phenyltriazolyl group (Scheme 7).

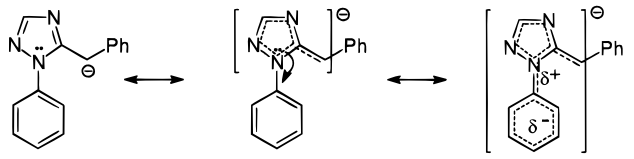
This result is due to the high fraction of negative charge delocalized onto the five-membered heterocycle from the adjacent carbanionic carbon. The 2p-electron pair of N(1) is inhibited for delocalization onto the

(21) It is possible that this different behavior is mainly due to the different acidity of the methylene bridges in phenylacetyl chloride and malonyl chloride. The primary amino group of **14** may be able to deprotonate the latter, thus giving rise to a very reactive ketene intermediate.

(22) Wakefield, B. J.; Wright, D. J. *Adv. Heterocycl. Chem.* **1979**, *125*, 147.

(23) (a) Fusco, R.; Rosnati, V.; Pagani, G. *Tetrahedron Lett.* **1966**, 1739−1744. (b) Fusco, R.; Rosnati, V.; Pagani, G. *Tetrahedron Lett.* **1967**, 4541−4544.

**Scheme 7**



heterocyclic ring but available for being pushed toward the phenyl ring, thus counteracting and relaxing the high charge strain on the small five-membered heterocycle. In the bis-activated system **11**$^-$, the fraction of the negative charge delocalized onto the heteroaromatic ring is smaller. The three nitrogen atoms per ring are thus capable of hosting the excess negative charge created upon deprotonation, and no pushing effect from the electron pair of the nitrogen atom to the *N*-phenyl ring is observed.

In short, the 1,2,4-triazol-5-yl group is highly ranked among the five- and six-membered aza-heterocycles. Its electron-withdrawing capacity is much greater than that of the weak 2-imidazolyl substituent because of the presence of a second pyridine-like nitrogen in an appropriate position. The determined charge demand is higher than that of oxazole, comparable with that of thiazole and pyridine, but still lower than that of diazines. We have shown that the −S− group in thiazolyl derivatives is electronically and magnetically equivalent to a −CH=CH− fragment, unlike the N(1) of imidazole, which strongly donates $\pi$-charge to the ring.[14a] Our results therefore converge toward the conclusion that the electron-withdrawing nature of the second pyridine-like nitrogen atom in 1,2,4-triazole almost exactly compensates the donor property of the pyrrole-like atom, thus making the triazolyl ring the electronic five-membered 'equivalent' of monoazines, such as pyridine.

## Experimental Section

$^{13}$C and $^{15}$N NMR spectra were recorded at 27 °C using a Bruker AMX-500 spectrometer operating at respectively 125.70 and 50.75 MHz and using 0.50 M solutions in DMSO. The spectral parameters and calibrations have been previously reported.[7] Anhydrous solvents were prepared by continuous distillation over sodium sand, in the presence of benzophenone and under nitrogen or argon, until the blue color of sodium ketyl was permanent. Extracts were dried over $Na_2SO_4$. The anions were prepared following a previously described procedure.[5] Melting points are uncorrected.

**Ethyl α-Amino-α-(phenylhydrazono)glyoxylate (14).** A mixture of concentrated ammonia (ca. 47 mmol, 3 mL) and dioxane (8 mL) was added dropwise to a solution of ethyl α-chloro-α-(phenylhydrazono)glyoxylate[26] in dioxane (30 mL). After the mixture was stirred for 8 h at room temperature, $NH_4Cl$ was filtered off and the solution dried. The solvent was removed under reduced pressure to give the crude product, which was purified by crystallization with toluene (2.16 g, 10.4 mmol, 69.3%): mp 125 °C (lit.[27] mp 128 °C); $^1$H NMR ($CDCl_3$) $\delta$ 7.23 (2 H, t), 7.09 (2 H, d), 6.88 (2 H, t), 6.64 (1 H, s), 4.51 (2 H, s), 4.34 (2 H, q), 1.38 (3 H, t).

**Bis(1*H*-3-ethoxycarbonyl-1-phenyl-1,2,4-triazol-5-yl)methane (15).** A solution of malonyl chloride (3.06 g, 21.7 mmol) in acetonitrile (20 mL) was added dropwise under a nitrogen atmosphere to a solution of **14** (9.00 g, 43.4 mmol) in the same solvent (80 mL). The reaction mixture was refluxed for 3 h, treated with an aqueous solution (700 mL) of stoichiometric $NaHCO_3$, and extracted with $CH_2Cl_2$ (4 × 400 mL). After the mixture was washed with $H_2O$ and the combined extracts were dried, the elimination of the solvent left a solid (7.95 g) that was taken up with ethanol (20 mL) to give the product as a white solid (0.81 g, 1.81 mmol, 8.4%): mp 158−159 °C; recrystallization (EtOH) gave an analytical sample with no increase in mp; $^1$H NMR ($CDCl_3$) $\delta$ 7.47 (10 H, s), 4.44 (4 H, q), 4.39 (2 H, s), 1.38 (6 H, t); $^1$H NMR (DMSO-$d_6$) $\delta$ 7.57−7.52 (6 H, m), 7.51−7.45 (4 H, m), 4.61 (2 H, s), 4.33 (4 H, q), 1.29 (6 H, t); $^{13}$C NMR ($CDCl_3$) $\delta$ 159.5 (C=O), 154.3 (C-3), 151.4 (C-5), 135.9 (C ipso), 130.1 (C para), 129.6 (C meta), 125.3 (C ortho), 62.0 ($OCH_2$), 25.1 (bridge $CH_2$), 14.2 ($CH_3$). Anal. Calcd for $C_{23}H_{22}N_6O_4$: C, 61.87; H, 4.97; N, 18.82. Found: C, 61.67; H, 4.93; N, 18.61.

**Bis(1*H*-3-carboxy-1-phenyl-1,2,4-triazol-5-yl)methane (16).** A suspension of **15** (1.26 g, 2.82 mmol) in 20% HCl (30 mL) was refluxed for 1 h. After the suspension was cooled to room temperature, half of the solvent was evaporated under reduced pressure, and then the white precipitate was collected, washed with water, and dried over $CaCl_2$, overnight at room temperature and then for a further 30 min at 70 °C, to afford the product (1.00 g, 2.56 mmol, 90.8%). Recrystallization ($H_2O$) gave an analytical sample: mp 202−203 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 7.49−7.54 (10 H, m), 4.59 (2 H, s). Anal. Calcd for $C_{19}H_{14}N_6$: C, 58.48; H, 3.61; N, 21.53. Found: C, 58.29; H, 3.88; N, 21.72.

**Bis(1*H*-1-phenyl-1,2,4-triazol-5-yl)methane (11).** Bis(1*H*-3-carboxy-1-phenyl-1,2,4-triazol-5-yl)methane (**16**) (0.51 g, 1.31 mmol) was heated in a Kugelrohr apparatus at 200 °C under vacuum until carbon dioxide evolved. The resulting solid (0.39 g) was submitted to a flash chromatography (MeOH−AcOEt 1:9) on silica gel to give **11** as a light oil (81 mg, 0.27 mmol, 21%): $^1$H NMR ($CDCl_3$) $\delta$ 7.96 (2 H, s), 7.40−7.50 (10 H, m), 4.31 (2 H, s); HRMS calcd for $C_{17}H_{14}N_6$ 302.1280, found 302.1250.

From the flash chromatography, a white byproduct was isolated, which was identified as the pure bis-cyanoamide **17** (142 mg): mp 188−189 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.00−7.50 (10 H, m), 6.50 (1 H, s), 5.52 (1 H, s), 4.90 (2 H, s); MS *m*/*z* 302 (M, 100), 77 (40); IR (Nujol) 2232 (CN). Anal. Calcd for $C_{17}H_{14}N_6$: C, 67.54; H, 4.66; N, 27.80. Found: C, 67.17; H, 5.01; N, 27.42.

**1*H*-1-phenyl-5-(*β*-styryl)-1,2,4-triazole (12).** Aqueous 50% NaOH (0.8 mL) was added dropwise to a solution of 1*H*-5-methyl-1-phenyl-1,2,4-triazole[28] (**19**) (0.50 g, 3.14 mmol) and benzaldehyde (0.50 g, 4.71 mmol) in DMSO (5 mL). After the mixture was stirred for 16 h at room temperature, another aliquot of benzaldehyde (0.17 g) in DMSO (1 mL) was added. After 40 h, the reaction mixture was poured into water (15 mL) and extracted with diethyl ether (4 × 10 mL); the organic layer was then washed with water (20 mL). The solvent was removed from the dried extracts to leave a yellowish oil (0.47 g) that was submitted to flash chromatography (AcOEt−hexane, 2:1) on silica gel to afford a mixture of the product and benzylic alcohol. The pure compound **12** (38 mg, 0.15 mmol, 5%) was obtained via its stifnate: mp 110−112 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.04 (1 H, s), 7.81 (1 H, d, $J_{\alpha,\beta}$ = 16.0), 7.30−7.60 (10 H, m), 6.89 (1 H, d). Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.87; H, 5.29; N, 17.09.

**1*H*-5-Benzyl-3-ethoxycarbonyl-1-phenyl-1,2,4-triazole (20).** A solution of phenylacetyl chloride (1.49 g, 9.65 mmol) in toluene (8 mL) was added dropwise under a nitrogen atmosphere to a hot solution of **14** (2.00 g, 9.65 mmol) in the same solvent (32 mL); the immediate formation of a precipitate was observed. The reaction mixture was refluxed for 4 h, and then the dark precipitate filtered off. The organic layer was washed with an aqueous solution of 5% NaOH (2 × 10 mL), dried, and evaporated under reduced pressure to leave the crude product as a light brown oil (2.24 g). The product was

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(25) Polya, J. B. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 5.
(26) Fusco R., Romani, R. *Gazz. Chim. Ital.* **1946**, *76*, 419−438.
(27) Bowack, D. A.; Lapworth, A. *J. Chem. Soc.* **1905**, *87*, 1854−1869.
(28) Micetich, R. G.; Spevak, P.; Hall, T. W.; Brins, B. K. *Heterocycles* **1985**, *23*, 1645−1649.

purified by chromatography on silica gel ($CH_2Cl_2$−AcOEt 9:1) to give **20** as a white solid (1.30 g, 4.23 mmol, 43.8%): mp 85−87 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.05−7.50 (10 H, m, aromatic protons), 4.51 (2 H, q, $J$ = 7.1), 4.20 (2 H, s,), 1.44 (3 H, t, $CH_3$). Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.47; H, 5.68; N, 13.45.

**1*H*-5-Benzyl-3-carboxy-1-phenyl-1,2,4-triazole (21).** A suspension of **20** (3.68 g, 11.97 mmol) in $H_2SO_4$ (40%, 60 mL) was refluxed for 2.5 h. After the suspension was cooled to room temperature, water (30 mL) was added, and the formation of a precipitate was observed. The white precipitate was collected, washed with water, and dried over $CaCl_2$, overnight at room temperature, to afford the product (2.67 g, 9.56 mmol, 79.9%). Recrystallization (EtOH−$H_2O$) gave an analytical sample: mp 81−82 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.54−7.43 (3 H, m), 7.36−7.30 (2 H, m), 7.28−7.20 (3 H, m), 7.12−7.06 (2 H, m), 4.30 (2 H, s). Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.04. Found: C, 68.54; H, 4.50; N, 15.32.

**1*H*-5-Benzyl-1-phenyl-1,2,4-triazole (13).** A mixture of **21** (2.50 g, 8.95 mmol) and electrolytic copper powder (2.5 g) was heated in a Kugelrohr apparatus at 175 °C at 0.03 mmHg. The distillation afforded the practically pure **13** (1.12 g, 4.76 mmol, 53.2%) as a white solid: mp = 52−55 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.00 (1 H, s), 7.10−7.45 (10 H, m), 4.16 (2 H, s); $^1$H NMR (DMSO-$d_6$) 8.10 (1 H, s), 7.60−7.45 (5 H, m), 7.30−7.15 (3 H, m), 7.12−7.04 (2 H, m), 4.20 (2 H, s); MS (EI) $m/z$ 235 ($M^{\bullet+}$; 51), 234 (100), 220 (31); HRMS $m/z$ calcd for $C_{15}H_{13}N_3$ 235.1109, found 235.1107; calcd for $C_{15}H_{12}N_3$ 234.1031, found 234.1029.

**Acknowledgment.** We would like to thank Dr. Fabio Nicolosi for his help in the preparation of the anion samples for NMR investigation.

**Supporting Information Available:** Copies of $^1$H ($CDCl_3$) and $^{13}$C NMR (DMSO-$d_6$) spectra of compound **11** and copies of $^1$H (DMSO-$d_6$) spectra (full and aromatic region) of compound **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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