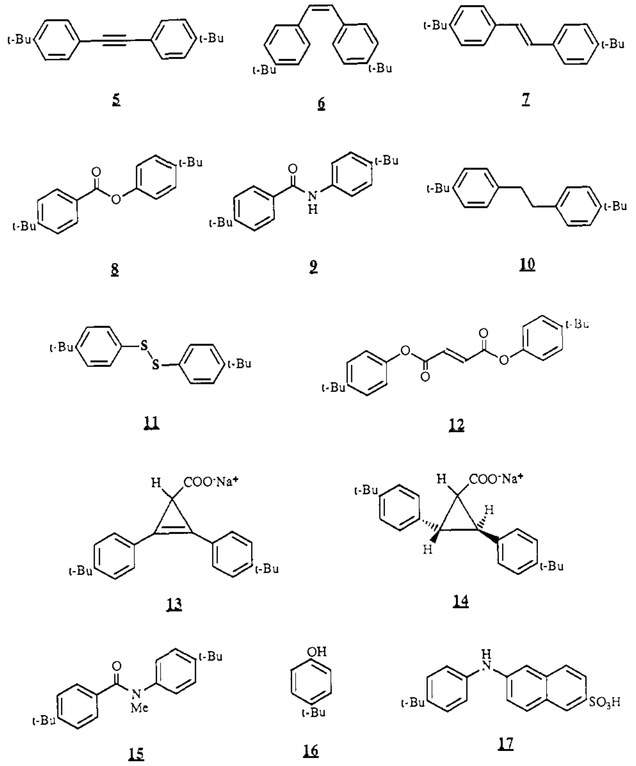
Chart I



Ethylene glycol was sometimes used to weaken the binding (m-t-butylphenyl acetate binds to β-cyclodextrin ca. 150 times more weakly in ethylene glycol than in water). As Table I shows, ester **8** and cyclopropene **13** are very strongly bound to **2**, with constants (water) exceeding 10^8 M^{-1}. Interestingly, amide **9** is considerably weaker and the disulfide **11** is somewhat weaker, while the overlong fumarate ester **12** and the crowded *cis*-stilbene **6** (but cf. the slightly less crowded cyclopropene derivative **13**) are only weakly bound.

In ethylene glycol solvent (Table I), the ester **8** is now a little over 10^4 times more weakly bound than in water, almost exactly what would be predicted for two *tert*-butylphenyl groups with this solvent change. The *trans*-stilbene **7**, the dihydrostilbene **10**, and the diarylacetylene **5** are comparable to the ester **8**, as is the *N*-methylamide **15**.

The diester **4** binds monodentate substrates with a normal ca. 10^4 M^{-1} constant but the bidentate cyclopropene substrate **13** quite strongly, twice as well (by direct competition) as does the dimer **2**. The secondary disulfide dimer **3**, by contrast, showed no enhanced binding; apparently the tight linkage crowds the system unduly.

Our largest binding constants of 10^8–10^9 are already similar to those of medium-affinity antibodies. With more rigid links between the cyclodextrins, the binding constants should be even higher. Dimer **4** carries a catalytic group that can direct chlorination.[10] Thus the potential for the use of such multiple binding in enzyme mimics seems very attractive.

Acknowledgment. Support of this work by the NIH and the ONR and a Chaim Weizmann Postdoctoral Fellowship to N.G. from the American Committee for the Weizmann Institute of Science are gratefully acknowledged.

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(7) We propose this acronym for 2-(p-*tert*-butylanilino)naphthalene-6-sulfonic acid. The compound is fluorescent when bound to a cyclodextrin, but not when unbound in solution.

(8) Prepared from 2-aminonaphthalene-6-sulfonic acid and p-*tert*-butylaniline under the Bucherer conditions used by Kosower[9] to synthesize analogous ANS derivatives.

(9) Kosower, E. M.; Dodiuk, H.; Tanizawa, K.; Ottolenghi, M.; Orbach, N. *J. Am. Chem. Soc.* **1975**, *97*, 2167.

(10) Breslow, R.; Guo, T. *Tetrahedron Lett.* **1987**, *28*, 3187.

Ethynol: A Theoretical Prediction of Remarkably High Gas-Phase Acidity

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Received April 26, 1989

In a recent communication that describes the first generation and direct observation of an ynol in solution,[1-3] Kresge, Wirz, and co-workers[1] noted that phenylynol ($PhC{\equiv}COH$) is more acidic than its enol analogue, $PhCH{=}CHOH$, by at least 7 pK_a units. This is a striking result and raises some interesting questions. One immediate point of interest is whether or not this result carries over to the gas phase, i.e., is it an intrinsic effect or is it a solvent effect?[4] A second point of interest concerns the origin of the high relative acidity of the ynol: is it largely due to some special stability of the ynolate anion or to some special instability of the neutral ynol? In order to address these questions, we have carried out ab initio molecular orbital calculations of the gas-phase acidities of the prototype enol ($CH_2{=}CHOH$) and ynol ($HC{\equiv}COH$) and related systems.

Standard ab initio molecular orbital calculations[5] were carried out with a modified version[6] of the Gaussian 86 system of programs.[7] Geometry optimizations were performed for all systems at the HF/6-31+G* level and improved relative energies obtained from MP4/6-311+G** calculations at these optimized geometries. Zero-point vibrational contributions to the relative energies were obtained from HF/6-31+G* vibrational frequencies, scaled by 0.9. Relevant energy data are presented in Table I and Figure 1.[8]

We begin our discussion by comparing several of the quantities that we have calculated with experimental or theoretical data from the literature. Our calculated energy difference between vinyl alcohol and acetaldehyde of 56 kJ mol^{-1} (Table I, reaction 1) is somewhat higher than a previous lower level theoretical value[9] of 45 kJ mol^{-1} and an experimental estimate[10] of 41 ± 8 kJ mol^{-1}. As far as we are aware, there is no experimental value for the energy difference between ethynol and ketene. We calculate a value of 155 kJ mol^{-1}, quite close to a previous lower level theoretical estimate (152 kJ mol^{-1}),[3] confirming that the ynol–ketene energy difference is significantly greater than the enol–keto energy

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(1) Chiang, Y.; Kresge, A. J.; Hochstrasser, R.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 2355.

(2) The first experimental evidence for the existence of a simple stable ynol ($HC{\equiv}COH$) in the gas phase was reported in the following: von Baar, B.; Weiske, T.; Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 282.

(3) The theoretical prediction of the stability in the gas-phase of ethynol was reported in the following: Bouma, W. J.; Nobes, R. H.; Radom, L.; Woodward, C. E. *J. Org. Chem.* **1982**, *47*, 1869.

(4) Examples of the reversal of the ordering of acidities or basicities in going from solution to the gas phase may be found in the following: Taft, R. W. In *Proton-Transfer Reactions*; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975.

(5) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(6) Nobes, R. H.; Smith, B. J.; Riggs, N. V.; Wong, M. W. Unpublished.

(7) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. *GAUSSIAN 86*; Carnegie-Mellon University: Pittsburgh, PA 15213.

(8) Optimized geometries and calculated total energies are available as supplementary material.

(9) Bouma, W. J.; Radom, L.; Rodwell, W. R. *Theor. Chim. Acta* **1980**, *56*, 149.

(10) (a) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648. (b) We note that, for the related pair of keto–enol systems, acetone and its enol ($CH_2{=}C(CH_3)OH$), two separate experiments yielded an energy difference of 58 ± 8 kJ mol^{-1}. See ref 10a and the following: Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4845.

0002-7863/89/1511-8297$01.50/0

Table I. Calculated Reaction Energies (kJ mol^{-1})^a

reaction	ΔE^b	ΔE^c	$\Delta E_{\text{exptl}}{}^d$
(1) $CH_3CH{=}O \rightarrow CH_2{=}CHOH$	54	56	41^e
(2) $CH_3CH{=}O \rightarrow CH_2{=}CHO^- + H^+$	1582	1548	1533
(3) $CH_2{=}CHOH \rightarrow CH_2{=}CHO^- + H^+$	1528	1491	1492
(4) $CH_2{=}C{=}O \rightarrow HC{\equiv}COH$	154	155	
(5) $CH_2{=}C{=}O \rightarrow HC{\equiv}CO^- + H^+$	1577	1545	1527
(6) $HC{\equiv}COH \rightarrow HC{\equiv}CO^- + H^+$	1423	1390	
(7) $CH_2{=}C{=}O + CH_2{=}CHO^- \rightarrow CH_3CH{=}O + HC{\equiv}CO^-$	-5	-3	-5
(8) $CH_3OH \rightarrow CH_3O^- + H^+$	1645	1606	1595
(9) $HC{\equiv}CF + CH_4 \rightarrow HC{\equiv}CH + CH_3F$	-41	-38	
(10) $HC{\equiv}COH + CH_4 \rightarrow HC{\equiv}CH + CH_3OH$	4	9	
(11) $HC{\equiv}CNH_2 + CH_4 \rightarrow HC{\equiv}CH + CH_3NH_2$	27	32	
(12) $CH_2{=}CHF + CH_4 \rightarrow CH_2{=}CH_2 + CH_3F$	29	34	
(13) $CH_2{=}CHOH + CH_4 \rightarrow CH_2{=}CH_2 + CH_3OH$	47	50	
(14) $CH_2{=}CHNH_2 + CH_4 \rightarrow CH_2{=}CH_2 + CH_3NH_2$	46	50	
(15) $HC{\equiv}CO^- + CH_4 \rightarrow HC{\equiv}CH + CH_3O^-$	227	225	
(16) $CH_2{=}CHO^- + CH_4 \rightarrow CH_2{=}CH_2 + CH_3O^-$	164	164	

^{a}HF/6-31+G* optimized structures. ^{b}MP4/6-311+G** values. ^{c}MP4/6-311+G** values together with (scaled) zero-point vibrational corrections. ^{d}Experimental values at 298 K, as quoted in ref 11 and 12 unless otherwise noted. ^{e}Reference 10.

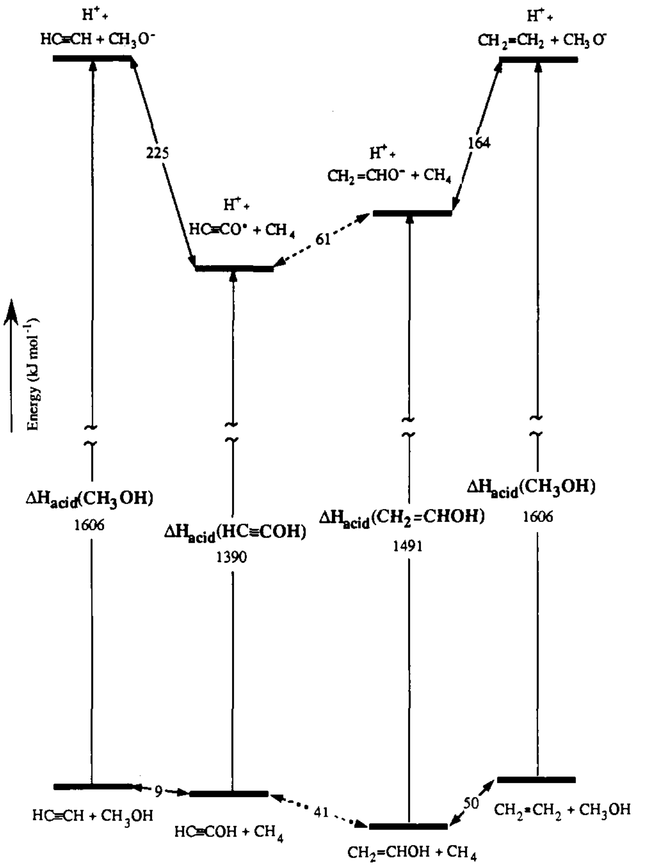

Figure 1. Schematic representation of calculated relative energies including calculated gas-phase acidities (ΔH_{acid}) (MP4/6-311+G** together with zero-point vibrational corrections).

difference found for the vinyl alcohol/acetaldehyde system.

Experimental gas-phase acidities of methanol, acetaldehyde, vinyl alcohol, and ketene are all available from literature data.[11,12] Our calculated values of 1606, 1548, 1491, and 1545 kJ mol^{-1}, respectively (Table I, reactions 8, 2, 3, and 5), are generally higher than the experimental values (1595, 1533, 1492, and 1527 kJ mol^{-1}, respectively), but the agreement is nevertheless very reasonable. One particularly pleasing aspect is that flowing-afterglow experiments[12] show that acetaldehyde is marginally less acidic (by 5 kJ mol^{-1}) than ketene, a result that is nicely reproduced by our calculations (which yield a difference in acidities of 3 kJ mol^{-1}). The good agreement between calculated and experimental acidities for these systems lends confidence to our predictions for ethynol for which appropriate gas-phase data are not presently available.

Our calculations predict gas-phase acidities of 1491 kJ mol^{-1} for vinyl alcohol (Table I, reaction 3) and 1390 kJ mol^{-1} for ethynol (reaction 6), i.e., ethynol is more acidic by 101 kJ mol^{-1}. Thus, we predict that, *in the gas phase as in solution, ethynol is substantially more acidic than vinyl alcohol.*[13]

To what can we attribute this greater acidity? In seeking a rationalization, we begin by comparing energies of interaction of some representative substituents with double and triple bonds, as given by bond separation energies (BSEs),[14] e.g.,

$$HC{\equiv}CX + CH_4 \rightarrow HC{\equiv}CH + CH_3X$$

It has previously been noted on this basis[15] that σ-electron withdrawal from the triple bond in $HC{\equiv}CX$ is quite unfavorable, whereas π-electron donation is quite favorable. Consistent with the ordering of σ-electron withdrawal ($F > OH > NH_2$) and π-electron donation ($NH_2 > OH > F$), we observe that the calculated BSE for $HC{\equiv}CF$ (reaction 9) is strongly negative, due largely to the unfavorable σ-electron interaction between the fluoro substituent and the triple bond, while the calculated BSE for $HC{\equiv}CNH_2$ (reaction 11) is strongly positive because of the favorable π-electron interaction. For the OH substituent, the unfavorable σ- and favorable π-effects are more nearly balanced, and the BSE for $HC{\equiv}COH$ is small and positive (reaction 10).

For doubly bonded systems $CH_2{=}CHX$, the σ-effect appears to be much less important and the variation in BSE with σ and π properties of the substituent is much less marked (reactions 12–14). Thus, whereas the BSEs for $HC{\equiv}CX$ range from −38 kJ mol^{-1} (for X = F) to +32 kJ mol^{-1} (X = NH_2), those for $CH_2{=}CHX$ lie in the much narrower range from +34 kJ mol^{-1} (X = F) to +50 kJ mol^{-1} (X = NH_2).

We now consider the species involved in comparing the acidities of ethynol and vinyl alcohol (reactions 6 and 3), beginning with the neutral acids, $HC{\equiv}COH$ and $CH_2{=}CHOH$. We have already noted that the BSE for $HC{\equiv}COH$ (9 kJ mol^{-1}) is significantly smaller than that for $CH_2{=}CHOH$ (50 kJ mol^{-1}) because of the destabilizing σ interaction of the OH group with the triple bond. This results in a relative destabilization of neutral $HC{\equiv}COH$ by 41 kJ mol^{-1} (Figure 1).

If we turn to the conjugate bases, we note initially that the O^- substituent is not only a strong π-electron donor but also a weak

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[11] Lias, S. G.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. F.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, Suppl. 1.

[12] Oakes, J. M.; Jones, M. E.; Bierbaum, V. M.; Ellison, G. B. *J. Phys. Chem.* **1983**, *87*, 4810.

[13] Interestingly, ethynol is predicted to be slightly more acidic in the gas phase than HCl, for which the acidity values are 1395 kJ mol^{-1} (experimental value from ref 11) and 1415 kJ mol^{-1} (MP4/6-311+G** with zero-point vibrational correction).

[14] Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

[15] Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.

σ-electron *donor*. The π and σ interactions are thus *both favorable* in $HC\equiv CO^-$, leading to a calculated BSE of 225 kJ mol^{-1}. For the double-bonded system $CH_2{=}CHO^-$, as pointed out above, the interaction energy is less sensitive to σ effects, and accordingly, the BSE, though still indicating a strongly stabilizing interaction, is somewhat lower, at 164 kJ mol^{-1}. There is thus a relative stabilization of the $HC\equiv CO^-$ anion by 61 kJ mol^{-1} (Figure 1).[16]

The combination of the relative destabilization of $HC\equiv COH$ (by 41 kJ mol^{-1}) and stabilization of $HC\equiv CO^-$ (by 61 kJ mol^{-1}) leads to the greater acidity of $HC\equiv COH$ compared with $CH_2{=}CHOH$ (by 101 kJ mol^{-1}). The schematic representation of these results (Figure 1) also presents the acidities of $HC\equiv COH$ and $CH_2{=}CHOH$ relative to a common standard, CH_3OH. This shows that $HC\equiv COH$ and $CH_2{=}CHOH$ are both substantially more acidic than CH_3OH, largely because of relative stabilization of the conjugate bases ($HC\equiv CO^-$ and $CH_2{=}CHO^-$).

Several important points emerge from this study.

1. The high relative acidity of ethynol ($HC\equiv COH$) that is observed in solution is predicted to carry over to the gas phase.
2. The high relative acidity of ethynol may be attributed partly to relative destabilization of neutral ethynol and partly to relative stabilization of the ynolate anion.
3. Acidities calculated for CH_3CHO, CH_2CHOH, CH_2CO, and CH_3OH at the MP4/6-311+G** level are generally somewhat higher than, but in reasonable agreement with, experimental values.

Acknowledgment. We gratefully acknowledge a generous allocation of computer time on the Fujitsu FACOM VP-100 of the Australian National University Supercomputer Facility.

Supplementary Material Available: Table II with calculated total energies and zero-point vibrational energies and Figure 2 with HF/6-31+G* optimized geometries (3 pages). Ordering information is given on any current masthead page.

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[16] Note that, in calculating the relative stabilizations, it is necessary for balance to include acetylene (for the triply bonded systems) or ethylene (for the doubly bonded systems); this is done for both the neutrals and anions and therefore, together with CH_3OH on the one hand and $CH_3O^- + H^+$ on the other, provides useful reference levels for comparison purposes.

Synthesis and Structure of Novel Polycyclic Species from Toluene and *m*-Xylene and the Dehalogenation Product of Difluoro(diisopropylamino)borane

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Received May 23, 1989

Reaction products obtained from aromatic compounds and the dehalogenated species formed upon treatment of dichloro(diisopropylamino)borane with active metals (Na/K) appear to be formed by carben(oidal) processes.[1-3] Indeed the formation of these polycyclic compounds in some respects resembles the valence isomerization in aromatic compounds which results from a tandem of carbenoid processes in the Katz reaction.[4] However, it differs from the Katz mechanism as hydrogen atom transfer is frequently observed in our reactions.[1,3] The three-dimensional species contain only three-coordinated boron and three- or four-coordinated carbon (sp^2 and sp^3 hybridization) and therefore are quite different from carboranes. It has been shown earlier that a *nido*-carborane structure is destabilized by amino substitution at the boron sites, giving a bicyclic structure.[5]

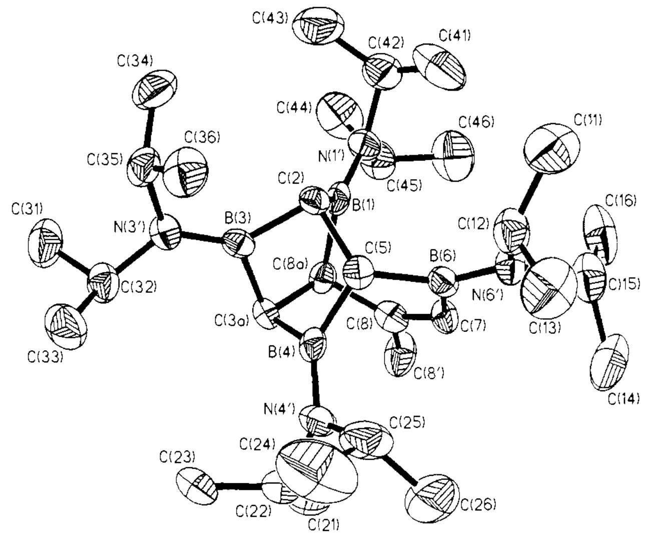


Figure 1. Structure of **1** (hydrogen atoms omitted) showing 40% probability thermal motion ellipsoids. Selected mean bond distances (Å) are as follows: B–C (mean) = 1.586 (9), N–C (mean) = 1.476 (14), C(8a)–C(8) = 1.518 (8), C(2)–C(5) = 1.642 (9), B–N (mean) = 1.404 (7), C(3a)–C(8a) = 1.596 (11), C(8)–C(7) = 1.335 (11), C(8)–C(8′) = 1.532 (8).

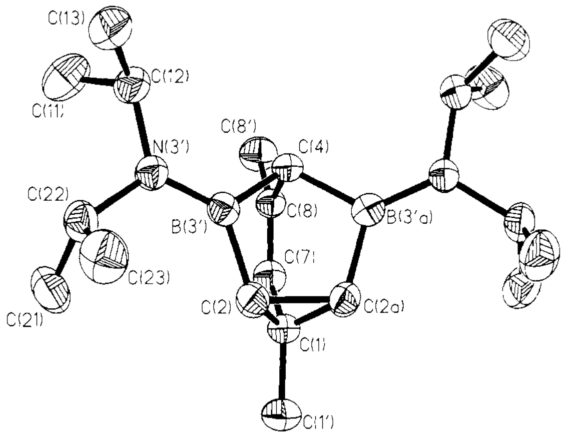
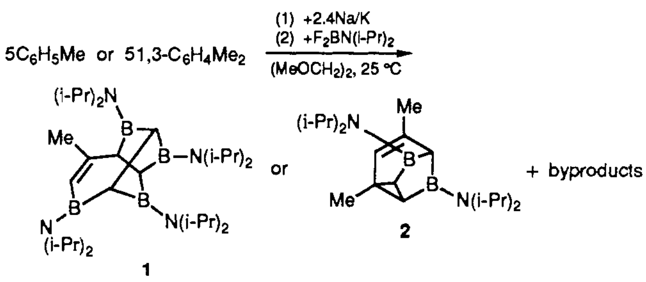


Figure 2. Structure of **2** (hydrogen atoms omitted) showing 40% probability thermal motion ellipsoids. C(1), C(1′), C(7), C(8), C(8′), and C(4) lie on a crystallographic mirror plane. Selected bond distances (Å) are as follows: B(3′)–N(3′) = 1.396 (4), C(4)–C(8) = 1.524 (5), C(8)–C(7) = 1.329 (6), C(1)–C(2) = 1.520 (4), C(1)–C(1′) = 1.502 (6), N(3)–C(12) = 1.471 (4), B(3′)–C(4) = 1.604 (3), C(8)–C(8′) = 1.506 (4), C(7)–C(1) = 1.487 (4), C(2)–C(2a) = 1.561 (5), C(2)–B(3′) = 1.563 (4), N(3′)–C(22) = 1.485 (3).

Scheme I



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[1] Meller, A.; Maringgele, W.; Elter, G.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1987**, *120*, 1437.

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[4] Burger, U.; Thorel, P. J.; Mentha, Y. *Chimia* **1987**, *41*, 26.

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