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# An ab initio study of electrophilic aromatic substitution*

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**Abstract.** Proton affinities are calculated at all reactive positions for the normal benzenoid hydrocarbons, benzene, naphthalene, phenanthrene and anthracene, a strained benzenoid hydrocarbon, biphenylene, and a nonalternant hydrocarbon, fluoranthene, and the results are compared to experimental protodetritiation rates. Methods used include PM3 and Hartree-Fock calculations at the STO-3G, 3-21G*, 6-31G* and MP2//6-31G* levels. Generally good agreement is found between theory and experiment with 6-31G* giving the best correlations.

**Key words:** Proton affinity – Protodetritiation – Protonation – Orientation – Alternant hydrocarbon

Polycyclic aromatic hydrocarbons(PAHs) have received increasing recent interest because of their ubiquitous environmental pollution, and because of carcinogenesis and mutagenesis [1, 2]. There is increasing evidence that carcinogenic/mutagenic activity which ultimately leads to PAH-DNA adduct formation is initiated by electrophilic and/or oxidation chemistry involving PAH carbocations or radical cations [3–7]. Protonated PAHs have long been known in solution and have been characterized, in particular, by NMR [4]. A number of protonated PAHs are also known in the gas phase and have provided the corresponding proton affinities. Protonated PAHs are also valuable models for interpreting electrophilic aromatic substitution [8]. Calculations of the corresponding $\pi$-molecular orbital (MO) systems provided early successes for the Hückel MO (HMO) method ("localization" energies) [8] in qualitative and quantitative applications to aromatic substitution. Approximation of these localization energies was the earliest application of Fukui's frontier electron approach [9, 10], an approach that is also related to Dewar's perturbation theory of aromatic substitution [11–13]. A number of theoretical approaches within the $\pi$-approximation have been suggested for quantitative correlations of electrophilic aromatic substitution but for benzenoid PAHs they are all mutually related and give similar correlations [8]. For other types of PAH, however, these HMO-based methods as well as a number of semiempirical MO approaches fail. For example, none of the methods give good correlations for the reactivity of different positions in fluoranthene [14, 15]. Similarly, although all HMO-based methods predict the $\beta$-position of biphenylene to be more reactive than the $\alpha$-position, in contrast to naphthalene, the magnitude of the orientation specificity is incorrect [16]. It seems clear that in many of these cases ring-strain effects play a role that is not accounted for by semiempirical $\pi$-electron methods. The purpose of this paper is to test whether ab initio methods can give a satisfactory account of models for aromatic substitution. The methods are applied to several normal benzenoid PAHs, an alternant but strained benzenoid PAH (biphenylene), and a nonalternant PAH, fluoranthene.

We chose to calculate the protonated PAHs because this would provide proton affinities (PAs) that could be compared with experimental values [17]; however, these PA values pertain only to the most stable protonated compound corresponding to the most reactive position, but they still serve to calibrate the calculations. Moreover, it has long been known that the rates of many electrophilic aromatic substitution reactions correlate well with equilibrium values for protonation in solution [8]. In particular, rates for protodetritiation are available for many positions on PAHs [15, 18, 19] and provide appropriate experimental data for testing with theory. The ab initio computations employed the Gaussian 92 and Gaussian 94 computer programs [20]. The structures of benzene, naphthalene, anthracene, phenanthrene, fluoranthene, biphenylene and their protonated carbocations were fully optimized at the HF/STO-3G, HF/3-21G* and HF/6-31G* levels with single-point calculations at the MP2/6-31G*//HF6-31G* level. The PAHs themselves have been optimized at the HF/6-31G* level previously [21], but the results are repeated here for convenience. Semiempirical calculations are available for many of the protonated derivatives [4, 22]. Total

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**Table 1.** The total electronic energies (hartree) calculated by PM3, HF/STO-3G, HF/3-21G*, HF/6-31G* and MP2//HF/6-31G* methods

| Molecule | PM3[a] | HF/STO-3G | HF/3-21G* | HF/6-31G* | MP2/6-31G*// HF/6-31G* |
|---|---|---|---|---|---|
| Benzene[b] | 0.037232 | −227.89136 | −229.41945 | −230.70314 | −231.45659 |
| Benzene-1 | 0.338458 | −228.26258 | −229.72218 | 231.01468 | −231.74813 |
| Naphthalene[b] | 0.064577 | −378.68685 | −381.21581 | −383.35505 | −384.61185 |
| Naphthalene-1 | 0.347288 | −379.08675 | −381.54283 | −383.69034 | −384.92764 |
| Naphthalene-2 | 0.352542 | −379.07896 | −381.53548 | −383.68433 | −384.92065 |
| Phenanthrene[b] | 0.087351 | −529.48745 | −533.01572 | −536.00976 | −537.77200 |
| Phenanthrene-1 | 0.366374 | −529.89137 | −533.34464 | −536.34758 | −538.09180 |
| Phenanthrene-2 | 0.370586 | −529.88538 | −533.33953 | −536.34399 | −538.08676 |
| Phenanthrene-3 | 0.368387 | −529.88949 | −533.34293 | −536.34718 | −538.08945 |
| Phenanthrene-4 | 0.370644 | −529.88877 | −533.34323 | −536.34646 | −538.09137 |
| Phenanthrene-9 | 0.365962 | −529.89276 | −533.34625 | −536.34941 | −538.09239 |
| Anthracene[b] | 0.097926 | −529.47248 | −533.00347 | −535.99877 | −537.76087 |
| Anthracene-1 | 0.370914 | −529.88760 | −533.34299 | −536.34688 | −538.08897 |
| Anthracene-2 | 0.377221 | −529.87913 | −533.33549 | −536.34103 | −538.08153 |
| Anthracene-9 | 0.357713 | −529.90840 | −533.36211 | −536.36428 | −538.10717 |
| Biphenylene[b,c] | 0.174737 | −453.41759 | −456.43787 | −459.01459 | −460.52364 |
| Biphenylene-1[c] | 0.462910 | −453.81098 | −456.75514 | −459.34383 | −460.83247 |
| Biphenylene-2[c] | 0.455292 | −453.82763 | −456.77224 | −459.36229 | −460.84779 |
| Fluoranthene | 0.127118 | −604.30325 | −608.32163 | −611.74562 | −613.76097 |
| Fluoranthene-1 | 0.406105 | −604.70907 | −608.65052 | −612.08474 | −614.07932 |
| Fluoranthene-2 | 0.411821 | −604.69911 | −608.64263 | −612.07689 | −614.07295 |
| Fluoranthene-3 | 0.400043 | −604.71961 | −608.66085 | −612.09488 | −614.08859 |
| Fluoranthene-7 | 0.406662 | −604.70468 | −608.64783 | −612.08138 | −614.08162 |
| Fluoranthene-8 | 0.403426 | −604.71161 | −608.65466 | −612.08914 | −614.08591 |

[a] $\Delta H_f^o$ at 25 °C in hartree
[b] These molecules have also been calculated at the STO-3G, 3-21G, 6-31G* levels in Ref. [21]
[c] These molecules have been calculated at the HF/6-31G* and MP2(fc)/6-31G*//HF/6-31G* levels in Ref. [24]

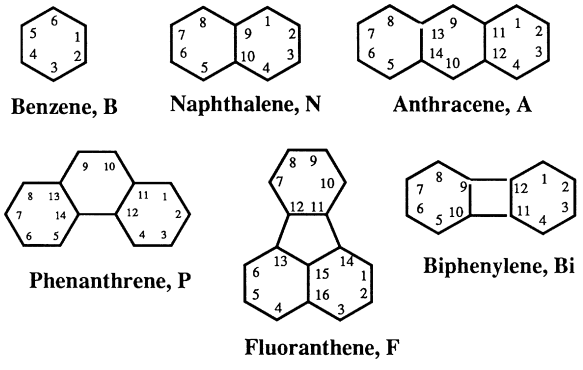



**Fig. 1.** The polycyclic aromatic hydrocarbons and the numbering system

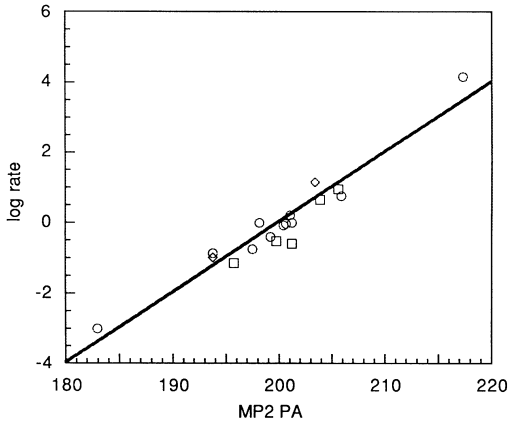



**Fig. 2.** Rates of protodetritiation compared to MP2/6-31G*//HF/6-31G* proton affinities. The *straight line* is based on the benzene, naphthalene, phenanthrene and anthracene (*BNPA*) points (*circles*), $-40.01 + 0.200x$, $R^2 = 0.953$. *Diamonds* are biphenylene; *squares* are fluoranthene

electronic energies (hartree) for these methods are listed in Table 1 for several PAHs and for the compounds protonated at the positions indicated by the number. The numbering systems are shown for convenience in Fig. 1. The calculated proton affinities of benzene, naphthalene, anthracene, phenanthrene, biphenylene and fluoranthene with the different basis sets are listed in Table 2, along with the logarithm values of relative protodetritiation rates [15, 18, 19] and experimental PA values [23].

For comparison purposes, calculations were also done with the semiempirical PM3 method. PM3 is parameterized to give $\Delta H_f^o$ at 25°C. To obtain the PA values the $\Delta H_f^o$ of $H^+$ was taken as the experimental value, 367.5 kcal mol$^{-1}$. As shown in Table 2, the values in column PM3 compare well with the experimental PA values, being low by an average of 2.8 kcal mol$-^{1}$ except for biphenylene. Some PA values have been determined previously using AM1 [22]. The ab initio results are not expected to reproduce the experimental PA results directly since the latter generally refer to temperatures about room temperature and the computed values pertain to 0 K. The MP2/6-31G*//HF/6-31G* calculations give values that are uniformly higher than experiment by 4.9 kcal mol$^{-1}$. Except for biphenylene, which deviates strongly from the trend of the other PAHs, the difference is 5.8 ± 1.7 kcal mol$^{-1}$. The 6-31G* results are higher than experiment by 17.8 ± 2.0 kcal mol$^{-1}$; biphenylene at this level is not markedly different from the other PAHs.

**Table 2.** The proton affinities of benzene, naphthalene, anthracene, phenanthrene, biphenylene, fluoranthene at different positions with several basis sets (kcal mol$^{-1}$)

| Aromatic position | Symbol[a] | PM3[b] | STO-3G | 3-21G* | 6-31G* | MP2 | Log relative rate[c] | Exp. proton affinity[d] |
|---|---|---|---|---|---|---|---|---|
| Benzene | B | 178.478 | 232.944 | 189.966 | 195.494 | 182.944 | −3.00 | 179.3 |
| Naphthalene-1 | 1N | 190.096 | 250.941 | 205.208 | 210.398 | 198.161 | (0) | 191.9 |
| Naphthalene-2 | 2N | 186.799 | 246.053 | 200.596 | 206.626 | 193.775 | −0.86 | |
| Phenanthrene-1 | 1P | 192.410 | 253.464 | 206.400 | 211.985 | 200.678 | −0.03 | |
| Phenanthrene-2 | 2P | 189.767 | 249.705 | 203.194 | 209.733 | 197.515 | −0.75 | |
| Phenanthrene-3 | 3P | 191.147 | 252.284 | 205.327 | 211.734 | 199.203 | −0.40 | |
| Phenanthrene-4 | 4P | 189.730 | 251.832 | 205.516 | 211.282 | 200.408 | −0.075 | |
| Phenanthrene-9 | 9P | 192.668 | 254.336 | 207.411 | 213.134 | 201.048 | 0.22 | 197.3 |
| Anthracene-1 | 1A | 196.198 | 260.492 | 213.052 | 218.442 | 205.886 | 0.76 | |
| Anthracene-2 | 2A | 192.240 | 255.177 | 208.346 | 214.771 | 201.217 | 0.00 | |
| Anthracene-9 | 9A | 204.482 | 273.544 | 225.050 | 229.361 | 217.307 | 4.17 | 209.7 |
| Biphenylene-1 | 1Bi | 186.669 | 246.856 | 199.090 | 206.601 | 193.794 | −0.97 | |
| Biphenylene-2 | 2Bi | 191.449 | 257.304 | 209.820 | 218.185 | 203.407 | 1.16 | 202.7 |
| Fluoranthene-1 | 1F | 192.433 | 254.656 | 206.382 | 212.801 | 199.768 | −0.52 | |
| Fluoranthene-2 | 2F | 188.846 | 248.406 | 201.431 | 207.875 | 195.770 | −1.14 | |
| Fluoranthene-3 | 3F | 196.237 | 261.270 | 212.864 | 219.164 | 205.585 | 0.96 | 198.0 |
| Flouranthene-7 | 7F | 192.083 | 251.901 | 204.694 | 210.693 | 201.211 | −0.59 | |
| Flouranthene-8 | 8F | 194.114 | 256.250 | 208.979 | 215.562 | 203.903 | 0.66 | |

[a] Position numbers from Fig. 1
[b] Values are derived from heats of formation at 25°C using experimental $\Delta H_f^o$ ($H^+$) = 367.5 kcal mol$^{-1}$ [23]
[c] Refs. [15, 18]
[d] Data are cited from Ref. [23]

The experimental PA results pertain to only the most reactive positions but protodetritiation rates are available for less reactive positions as well. The experimental rates correlate well with the MP2/6-31G*//HF/6-31G* values for simple alternant benzenoid systems, benzene, naphthalene, phenanthrene and anthracene (BNPA) (Fig. 2) as expected from the general correlation of such positions with all MO methods. Most important, however, is that the biphenylene and fluoranthene positions correlate almost as well as the "normal" positions; a linear regression based on all of the points, $-39.81 + 0.199x$ ($R^2 = 0.921$) is similar to the BNPA points alone. The largest deviation is for the fluoranthene 7-position which is 3.5 times less reactive than predicted by the BNPA correlation. This might reflect a steric hindrance effect at this position so that the rate of protonation does not in this case correlate with equilibrium protonation; however, the 4-position of phenanthrene with a similar steric situation correlates quite well and steric effects in protodetritiations are known to be small [25]. The order of reactivity of fluoranthene positions in nitration has been shown to be $3 > 8 > 7 > 1 > 2$ [14] in agreement with the calculated proton affinities; the difference from the order of protodetritiation reactivities is just a reversal of the 7- and 1-positions. The result may be an artifact of the basis set level; we note that the MP2 correction of the 6-31G* energies is greatest for the 7-position of all the protonated fluoranthenes.

The 6-31G* results give a correlation that is at least as good (Fig. 3). The biphenylene and fluoranthene points fit the BNPA correlation even better than the MP2 calculations and, in particular, the fluoranthene 7-position is no longer aberrant. A linear correlation based on all points is $-42.156 + 0.198x$ ($R^2 = 0.935$). Indeed, even the rather low level 3-21G* method does quite well as

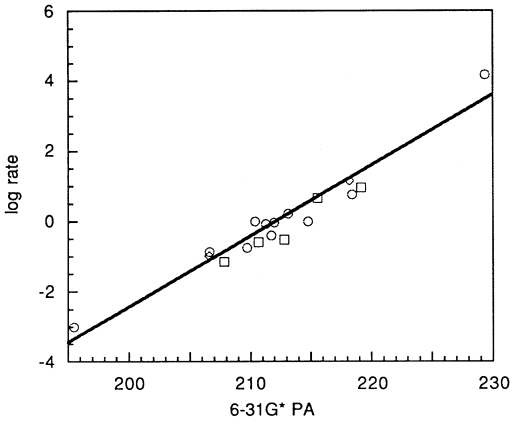



**Fig. 3.** Rates of protodetritiation compared to 6-31G*//HF/6-31G* proton affinities. The *straight line* is based on the BNPA points (*circles*), $-42.82 + 0.202x$, $R^2 = 0.947$. *Diamonds* are biphenylene; *squares* are fluoranthene

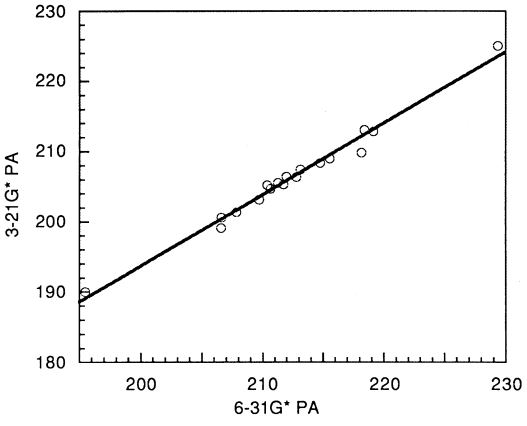



**Fig. 4.** 3-21G* Proton affinities compared to 6-31G* values. The regression line is $-10.474 + 1.020x$, $R^2 = 0.985$

**Table 3.** Selected bond lengths and bond angles of neutral and protonated PAHs

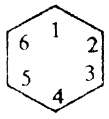
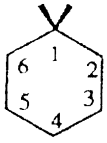
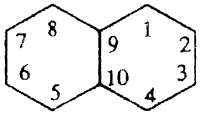
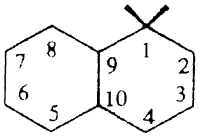
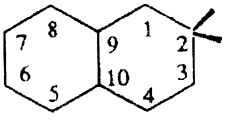
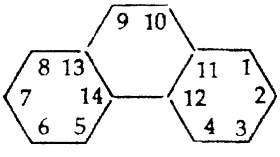
| Molecule | Bond length, Å | | | Bond angle, degrees | | |
|---|---|---|---|---|---|---|
| | Bond | Bond length | % change | Angle | Bond angle | % change |
|  Benzene | C1—C2[a,b] | 1.387 | | C2—C1—C6 | 120.000 | |
| | C1—H | 1.076 | | | | |
|  B | C1—C2 | 1.478 | 6.56 | C2—C1—C6 | 115.717 | −3.57 |
| | C2—C3 | 1.353 | −2.45 | C1—C2—C3 | 121.785 | 1.49 |
| | C3—C4 | 1.410 | 1.66 | C2—C3—C4 | 118.533 | −1.22 |
| | C1—H | 1.094 | 1.67 | C3—C4—C5 | 123.646 | 3.04 |
| | C2—H | 1.075 | −0.09 | | | |
| | C3—H | 1.073 | −0.28 | | | |
| | C4—H | 1.076 | 0.0 | | | |
|  Naphthalene | C1—C2[b,c] | 1.358 | | C2—C1—C9 | 120.775 | |
| | C2—C3 | 1.417 | | C1—C2—C3 | 120.255 | |
| | C1—C9 | 1.421 | | C1—C9—C10 | 118.970 | |
| | C9—C10 | 1.409 | | | | |
| | C1—H | 1.076 | | | | |
| | C2—H | 1.075 | | | | |
|  1N | C1—C2 | 1.483 | 9.20 | C2—C1—C9 | 115.706 | −4.20 |
| | C2—C3 | 1.349 | −4.80 | C1—C2—C3 | 123.003 | 2.29 |
| | C3—C4 | 1.413 | 4.05 | C2—C3—C4 | 118.746 | −1.25 |
| | C4—C10 | 1.400 | −1.48 | C3—C4—C10 | 123.925 | 2.61 |
| | C1—C9 | 1.500 | 5.56 | C4—C10—C9 | 119.045 | 0.06 |
| | C9—C10 | 1.416 | 0.50 | C1—C9—C10 | 119.574 | 0.51 |
| | C1—H | 1.090 | 1.30 | | | |
| | C2—H | 1.075 | 0.0 | | | |
| | C3—H | 1.073 | −0.19 | | | |
| | C4—H | 1.076 | 0.0 | | | |
|  2N | C1—C2 | 1.477 | 8.76 | C2—C1—C9 | 123.079 | 1.91 |
| | C2—C3 | 1.488 | 5.01 | C1—C2—C3 | 114.967 | −4.40 |
| | C3—C4 | 1.331 | −1.99 | C2—C3—C4 | 122.040 | 1.48 |
| | C4—C10 | 1.449 | 1.97 | C3—C4—C10 | 120.950 | 0.14 |
| | C1—C9 | 1.362 | −4.15 | C4—C10—C9 | 119.993 | 0.86 |
| | C9—C10 | 1.441 | 2.27 | C1—C9—C10 | 118.970 | 0.0 |
| | C1—H | 1.076 | 0.0 | | | |
| | C2—H | 1.092 | 1.58 | | | |
| | C3—H | 1.074 | −0.09 | | | |
| | C4—H | 1.074 | −0.19 | | | |
|  Phenanthrene | C1—C2[b,d] | 1.366 | | C2—C1—C11 | 121.014 | |
| | C2—C3[e] | 1.402 | | C1—C2—C3 | 119.470 | |
| | C3—C4 | 1.368 | | C2—C3—C4 | 120.386 | |
| | C4—C12 | 1.411 | | C3—C4—C12 | 121.370 | |
| | C1—C11 | 1.409 | | C1—C11—C12 | 119.837 | |
| | C11—C12 | 1.404 | | C4—C12—C11 | 117.924 | |
| | C10—C11 | 1.441 | | C9—C10—C11 | 121.098 | |
| | C9—C10 | 1.339 | | C10—C11—C12 | 119.811 | |
| | C12—C14 | 1.461 | | C11—C12—C14 | 119.091 | |
| | C1—H | 1.076 | | | | |
| | C2—H | 1.075 | | | | |
| | C3—H | 1.075 | | | | |
| | C4—H | 1.072 | | | | |
| | C9—H | 1.076 | | | | |

**Table 3** (Contd.)

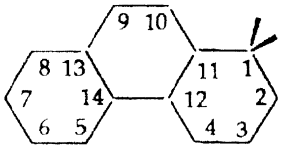
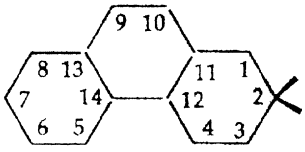
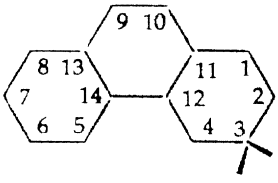
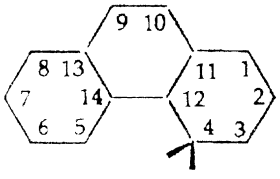
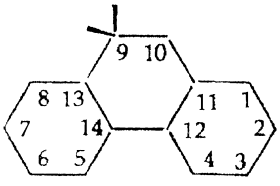
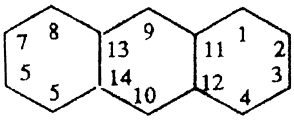
| Molecule | Bond length, Å | | | Bond angle, degrees | | |
|---|---|---|---|---|---|---|
| | Bond | Bond length | % change | Angle | Bond angle | % change |
|  1P | C1—C2 | 1.482 | 8.49 | C2—C1—C11 | 116.262 | −3.93 |
| | C2—C3 | 1.340 | −4.42 | C1—C2—C3 | 121.670 | 1.84 |
| | C3—C4 | 1.425 | 4.17 | C2—C3—C4 | 119.266 | −0.93 |
| | C4—C12 | 1.387 | −1.70 | C3—C4—C12 | 124.921 | 2.93 |
| | C1—C11 | 1.498 | 6.32 | C1—C11—C12 | 120.511 | 0.56 |
| | C11—C12 | 1.416 | 0.85 | C4—C12—C11 | 117.370 | −0.47 |
| | C1—H | 1.090 | 1.30 | | | |
| | C2—H | 1.075 | 0.0 | | | |
| | C3—H | 1.073 | −0.19 | | | |
| | C4—H | 1.073 | 0.09 | | | |
|  2P | C1—C2 | 1.476 | 8.05 | C2—C1—C11 | 123.769 | 2.28 |
| | C2—C3 | 1.482 | 5.71 | C1—C2—C3 | 114.126 | −4.47 |
| | C3—C4 | 1.334 | −2.49 | C2—C3—C4 | 122.396 | 1.67 |
| | C4—C12 | 1.448 | 2.62 | C3—C4—C12 | 121.532 | 0.13 |
| | C1—C11 | 1.354 | −3.90 | C1—C11—C12 | 119.426 | −0.34 |
| | C11—C12 | 1.445 | 2.92 | C4—C12—C11 | 118.752 | 0.70 |
| | C1—H | 1.076 | 0.0 | | | |
| | C2—H | 1.092 | 1.58 | | | |
| | C3—H | 1.075 | 0.0 | | | |
| | C4—H | 1.069 | −0.28 | | | |
|  3P | C1—C2 | 1.332 | −2.49 | C2—C1—C11 | 121.186 | 0.14 |
| | C2—C3 | 1.484 | 5.85 | C1—C2—C3 | 121.489 | 1.69 |
| | C3—C4 | 1.481 | 8.26 | C2—C3—C4 | 114.917 | −4.54 |
| | C4—C12 | 1.353 | −4.11 | C3—C4—C12 | 124.228 | 2.35 |
| | C1—C11 | 1.446 | 2.63 | C1—C11—C12 | 120.698 | 0.72 |
| | C11—C12 | 1.448 | 3.13 | C4—C12—C11 | 117.482 | −0.37 |
| | C1—H | 1.074 | −0.19 | | | |
| | C2—H | 1.075 | 0.0 | | | |
| | C3—H | 1.092 | 1.58 | | | |
| | C4—H | 1.073 | 0.09 | | | |
|  4P | C1—C2 | 1.419 | 3.88 | C2—C1—C11 | 124.511 | 2.89 |
| | C2—C3 | 1.342 | −4.28 | C1—C2—C3 | 118.355 | −0.93 |
| | C3—C4 | 1.484 | 8.48 | C2—C3—C4 | 122.510 | 1.76 |
| | C4—C12 | 1.500 | 6.31 | C3—C4—C12 | 116.508 | −4.01 |
| | C1—C11 | 1.392 | −1.21 | C1—C11—C12 | 119.160 | −0.56 |
| | C11—C12 | 1.408 | 0.28 | C4—C12—C11 | 118.956 | 0.88 |
| | C1—H | 1.076 | 0.0 | | | |
| | C2—H | 1.073 | −0.19 | | | |
| | C3—H | 1.075 | 0.0 | | | |
| | C4—H | 1.090 | 1.68 | | | |
|  9P | C9—C10 | 1.472 | 9.93 | C9—C10—C11 | 123.838 | 2.26 |
| | C10—C11 | 1.360 | −5.62 | C10—C11—C12 | 119.895 | 0.07 |
| | C11—C12 | 1.445 | 2.92 | C11—C12—C14 | 120.123 | 0.87 |
| | C12—C14 | 1.462 | 0.07 | C12—C14—C13 | 119.704 | 0.51 |
| | C9—C13 | 1.501 | 4.16 | C10—C9—C13 | 115.352 | −4.74 |
| | C13—C14 | 1.400 | −0.28 | C9—C13—C14 | 121.087 | 1.07 |
| | C9—H | 1.091 | 1.39 | | | |
| | C10—H | 1.076 | 0.0 | | | |
|  Anthracene | C1—C2[b,d] | 1.348 | | C2—C1—C11 | 120.904 | |
| | C2—C3[f] | 1.433 | | C1—C2—C3 | 120.485 | |
| | C1—C11 | 1.436 | | C1—C11—C12 | 118.611 | |
| | C11—C12 | 1.425 | | C9—C11—C12 | 119.241 | |
| | C9—C11 | 1.389 | | C11—C9—C13 | 121.517 | |
| | C1—H | 1.076 | | | | |
| | C2—H | 1.075 | | | | |
| | C9—H | 1.077 | | | | |

**Table 3** (Contd.)

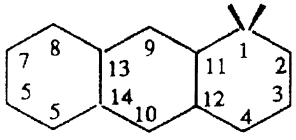
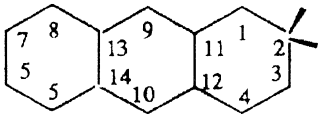
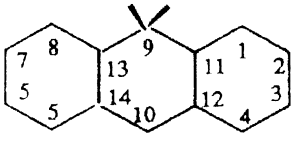
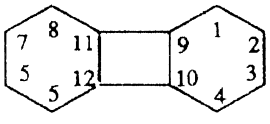
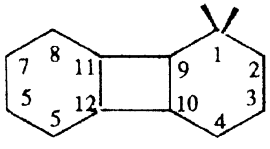
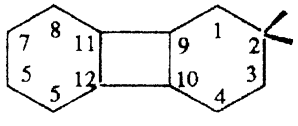
| Molecule | Bond length, Å | | | Bond angle, degrees | | |
|---|---|---|---|---|---|---|
| | Bond | Bond length | % change | Angle | Bond angle | % change |
|  1A | C1—C2 | 1.489 | 10.46 | C2—C1—C11 | 115.244 | −4.68 |
| | C2—C3 | 1.346 | −6.07 | C1—C2—C3 | 123.707 | 2.67 |
| | C3—C4 | 1.419 | 5.27 | C2—C3—C4 | 118.995 | −1.24 |
| | C4—C12 | 1.391 | −3.13 | C3—C4—C12 | 123.427 | 2.09 |
| | C1—C11 | 1.508 | 5.01 | C1—C11—C12 | 118.813 | 0.17 |
| | C11—C12 | 1.440 | 1.05 | C4—C12—C11 | 119.814 | 1.01 |
| | C1—H | 1.089 | 1.21 | | | |
| | C2—H | 1.076 | 0.09 | | | |
| | C3—H | 1.073 | −0.19 | | | |
| | C4—H | 1.076 | 0.0 | | | |
|  2A | C1—C2 | 1.481 | 9.87 | C2—C1—C11 | 123.023 | 1.75 |
| | C2—C3 | 1.496 | 4.40 | C1—C2—C3 | 114.398 | −5.05 |
| | C3—C4 | 1.326 | −1.63 | C2—C3—C4 | 122.557 | 1.72 |
| | C4—C12 | 1.460 | 1.67 | C3—C4—C12 | 121.614 | 0.59 |
| | C1—C11 | 1.359 | −5.36 | C1—C11—C12 | 120.109 | 1.26 |
| | C11—C12 | 1.454 | 2.04 | C4—C12—C11 | 118.299 | −0.26 |
| | C1—H | 1.077 | 0.09 | | | |
| | C2—H | 1.091 | 1.49 | | | |
| | C3—H | 1.074 | −0.09 | | | |
| | C4—H | 1.074 | −0.19 | | | |
|  9A | C9—C11 | 1.504 | 8.28 | C9—C11—C12 | 120.547 | 1.10 |
| | C11—C12 | 1.412 | −0.91 | C10—C12—C11 | 119.202 | −0.03 |
| | C10—C12 | 1.404 | 1.08 | C12—C10—C14 | 124.386 | 2.36 |
| | C9—H | 1.088 | 1.02 | C11—C9—C13 | 116.114 | −4.45 |
| | C10—H | 1.077 | 0.0 | | | |
|  Biphenylene | C1—C2 | 1.418 | | C2—C1—C9 | 115.698 | |
| | C2—C3 | 1.373 | | C1—C2—C3 | 121.866 | |
| | C1—C9 | 1.356 | | C1—C9—C10 | 122.436 | |
| | C9—C10 | 1.414 | | C10—C9—C11 | 90.000 | |
| | C9—C11 | 1.507 | | | | |
| | C1—H | 1.075 | | | | |
| | C2—H | 1.075 | | | | |
|  1Bi | C1—C2 | 1.509 | 6.42 | C2—C1—C9 | 110.873 | −4.17 |
| | C2—C3 | 1.332 | −2.99 | C1—C2—C3 | 123.485 | 1.33 |
| | C3—C4 | 1.469 | 3.60 | C2—C3—C4 | 122.466 | 0.49 |
| | C4—C10 | 1.337 | −1.40 | C3—C4—C10 | 117.511 | 1.57 |
| | C1—C9 | 1.471 | 8.48 | C1—C9—C10 | 123.340 | 0.74 |
| | C9—C10 | 1.428 | 0.99 | C4—C10—C9 | 122.324 | −0.09 |
| | C9—C11 | 1.434 | −4.84 | C10—C9—C11 | 92.195 | 2.44 |
| | C1—H | 1.091 | 1.49 | C9—C10—C12 | 87.363 | −2.93 |
| | C2—H | 1.074 | −0.09 | | | |
| | C3—H | 1.073 | −0.19 | | | |
| | C4—H | 1.074 | −0.09 | | | |
|  2Bi | C1—C2 | 1.504 | 6.06 | C2—C1—C9 | 116.928 | 1.06 |
| | C2—C3 | 1.499 | 9.18 | C1—C2—C3 | 116.125 | −4.71 |
| | C3—C4 | 1.356 | −4.37 | C2—C3—C4 | 125.719 | 3.16 |
| | C4—C10 | 1.403 | 3.47 | C3—C4—C10 | 114.156 | −1.33 |
| | C1—C9 | 1.319 | −2.73 | C1—C9—C10 | 123.380 | 0.77 |
| | C9—C10 | 1.459 | 3.18 | C4—C10—C9 | 123.690 | 1.02 |
| | C9—C11 | 1.499 | −0.53 | C10—C9—C11 | 87.006 | −3.33 |
| | C1—H | 1.074 | −0.09 | C9—C10—C12 | 91.041 | 1.16 |
| | C2—H | 1.090 | 1.40 | | | |
| | C3—H | 1.076 | 0.09 | | | |
| | C4—H | 1.073 | −0.19 | | | |

**Table 3** (Contd.)

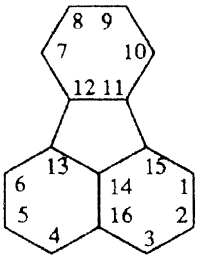
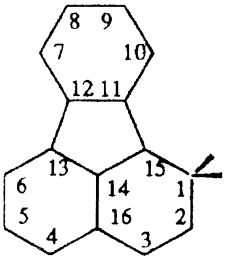
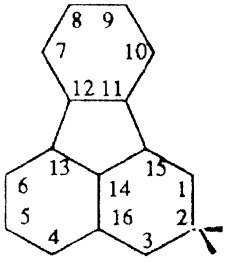
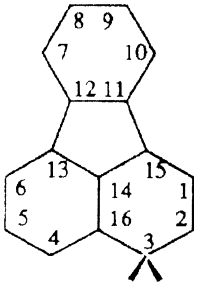
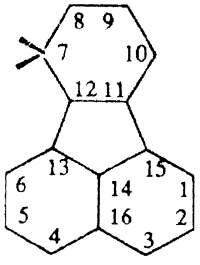
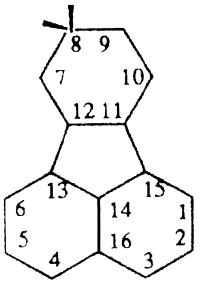
| Molecule | Bond length, Å | | | Bond angle, degrees | | |
|---|---|---|---|---|---|---|
| | Bond | Bond length | % change | Angle | Bond angle | % change |
|  Fluoranthene | C1—C15 | 1.360 | | C14—C15—C1 | 118.589 | |
| | C1—C2 | 1.424 | | C15—C1—C2 | 118.557 | |
| | C2—C3 | 1.365 | | C1—C2—C3 | 122.450 | |
| | C3—C16 | 1.423 | | C2—C3—C16 | 120.023 | |
| | C1—C15 | 1.413 | | C15—C14—C16 | 124.215 | |
| | C15—C14 | 1.383 | | C3—C16—C14 | 116.166 | |
| | C11—C15 | 1.481 | | C13—C14—C15 | 111.569 | |
| | C11—C12 | 1.411 | | C11—C15—C14 | 106.010 | |
| | C7—C12 | 1.379 | | C15—C11—C12 | 108.206 | |
| | C7—C8 | 1.391 | | C7—C12—C11 | 120.380 | |
| | C8—C9 | 1.385 | | C12—C7—C8 | 118.922 | |
| | C1—H | 1.076 | | C7—C8—C9 | 120.697 | |
| | C2—H | 1.076 | | | | |
| | C3—H | 1.076 | | | | |
| | C7—H | 1.076 | | | | |
| | C12—H | 1.075 | | | | |
|  1F | C1—C15 | 1.481 | 8.90 | C14—C15—C1 | 119.825 | 1.04 |
| | C1—C2 | 1.504 | 5.62 | C15—C1—C2 | 113.615 | −4.17 |
| | C2—C3 | 1.333 | −2.34 | C1—C2—C3 | 124.184 | 1.42 |
| | C3—C16 | 1.456 | 2.32 | C2—C3—C16 | 120.294 | 0.23 |
| | C1—C15 | 1.385 | −1.98 | C15—C14—C16 | 124.381 | 0.13 |
| | C15—C14 | 1.395 | 0.87 | C3—C16—C14 | 117.700 | 1.32 |
| | C11—C15 | 1.452 | −1.96 | C11—C15—C14 | 108.168 | 2.04 |
| | C14—C13 | 1.419 | 0.42 | C13—C14—C15 | 110.960 | −0.55 |
| | C1—H | 1.091 | 1.39 | C15—C11—12 | 107.823 | −0.35 |
| | C2—H | 1.075 | −0.09 | | | |
| | C3—H | 1.074 | −0.19 | | | |
|  2F | C1—C15 | 1.335 | −1.84 | C14—C15—C1 | 118.392 | −0.17 |
| | C1—C2 | 1.497 | 5.13 | C15—C1—C2 | 120.331 | 1.50 |
| | C2—C3 | 1.486 | 8.86 | C1—C2—C3 | 117.187 | −4.30 |
| | C3—C16 | 1.363 | −4.22 | C2—C3—C16 | 122.267 | 1.87 |
| | C1—C15 | 1.441 | 1.98 | C15—C14—C16 | 125.827 | 1.30 |
| | C15—C14 | 1.413 | 2.17 | C3—C16—C14 | 115.996 | −0.15 |
| | C11—C15 | 1.481 | 0.0 | C11—C15—C14 | 105.541 | −0.44 |
| | C14—C13 | 1.394 | −1.34 | C1—C15—C8 | 110.874 | −0.62 |
| | C1—H | 1.075 | −0.09 | C1—C14—C9 | 108.408 | 0.19 |
| | C2—H | 1.077 | 1.58 | | | |
| | C3—H | 1.093 | 0.09 | | | |
|  3F | C1—C15 | 1.418 | 4.26 | C14—C15—C1 | 120.146 | 1.31 |
| | C1—C2 | 1.351 | −5.13 | C15—C1—C2 | 117.544 | −0.85 |
| | C2—C3 | 1.497 | 9.67 | C1—C2—C3 | 125.548 | 2.53 |
| | C3—C16 | 1.499 | 5.34 | C2—C3—C16 | 114.745 | −4.40 |
| | C1—C15 | 1.427 | 0.99 | C15—C14—C16 | 124.676 | 0.37 |
| | C15—C14 | 1.372 | −0.80 | C3—C16—C14 | 117.341 | 1.01 |
| | C11—C15 | 1.442 | −2.63 | C11—C15—C14 | 107.318 | 1.23 |
| | C14—C13 | 1.404 | −0.64 | C1—C15—C8 | 110.565 | −0.90 |
| | C1—H | 1.073 | −0.28 | C1—C14—C9 | 110.310 | −0.91 |
| | C2—H | 1.076 | 0.0 | | | |
| | C3—H | 1.090 | 1.30 | | | |
|  7F | C7—C12 | 1.484 | 7.61 | C12—C7—C8 | 114.335 | −3.86 |
| | C7—C8 | 1.493 | 7.33 | C7—C8—C9 | 122.514 | 1.51 |
| | C8—C9 | 1.336 | −3.54 | C8—C9—C10 | 120.221 | −0.39 |
| | C9—C10 | 1.442 | 3.67 | C9—C10—C11 | 122.169 | 2.73 |
| | C10—C11 | 1.363 | −1.16 | C7—C12—C11 | 121.264 | 0.73 |
| | C11—C12 | 1.422 | 0.78 | C10—C11—C12 | 119.496 | −0.73 |
| | C12—C13 | 1.421 | −4.05 | C11—C12—C13 | 108.917 | 0.66 |
| | C11—C15 | 1.476 | −0.34 | C12—C11—C15 | 107.842 | −0.34 |
| | C7—H | 1.091 | 1.39 | | | |
| | C81—H | 1.074 | −0.09 | | | |
| | C9—H | 1.073 | −0.19 | | | |
| | C10—H | 1.076 | 0.0 | | | |

**Table 3** (Contd.)

| Molecule | Bond length, Å | | | Bond angle, degrees | | |
|---|---|---|---|---|---|---|
| | Bond | Bond length | %change | Angle | Bond angle | %change |
|  | C7—C12 | 1.336 | −3.12 | C12—C7—C8 | 121.304 | 2.00 |
| | C7—C8 | 1.489 | 7.05 | C7—C8—C9 | 115.518 | −4.29 |
| | C8—C9 | 1.488 | 7.44 | C8—C9—C10 | 123.199 | 2.07 |
| | C9—C10 | 1.342 | −3.52 | C9—C10—C11 | 118.474 | −0.38 |
| | C10—C11 | 1.425 | 3.34 | C7—C12—C11 | 119.830 | −0.46 |
| | C11—C12 | 1.460 | 3.47 | C10—C11—C12 | 121.675 | 1.08 |
| | C12—C13 | 1.479 | −0.14 | C11—C12—C13 | 107.075 | −1.05 |
| | C11—C15 | 1.419 | −4.19 | C12—C11—C15 | 108.349 | 0.13 |
| | C7—H | 1.075 | −0.09 | | | |
| | C81—H | 1.091 | 1.49 | | | |
| | C9—H | 1.075 | 0.0 | | | |
| | C10—H | 1.073 | −0.28 | | | |
| 8F | | | | | | |

[a] Experimental bond lengths: Ref. [26]
[b] Experimental bond lengths: Ref. [27]
[c] Experimental bond lengths: Ref. [28]
[d] Experimental bond lengths: Ref. [29]
[e] Bond lengths of neutral phenanthrene have also been calculated at the HF/STO-3G level: Ref. [30]
[f] Experimental results: Ref. [31]

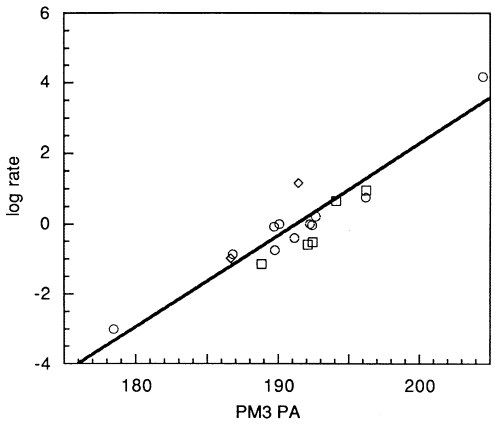



**Fig. 5.** Rates of protodetritiation compared to PM3 proton affinities. The *straight line* is based on the BNPA points (*circles*), $-49.99 + 0.261x$, $R^2 = 0.942$. *Diamonds* are biphenylene; *squares* are fluoranthene

indicated by comparison of 3-21G* and 6-31G* proton affinities in Fig. 4. Correspondingly, correlation of the logarithm of the relative rates for protodetritiation with 3-21G* proton affinities gives a regression of $-40.52 + 0.196x$ ($R^2 = 0.967$) for the BNPA points and $-40.03 + 0.194x$ ($R^2 = 0.945$) for all the points.

The lowest ab initio level, STO-3G, gives a good correlation for the BNPA positions ($-42.657 + 0.169x$; $R^2 = 0.952$) but does significantly more poorly when biphenylene and fluoranthene points are included ($-42.547 + 0.168x$; $R^2 = 0.922$). The semiempirical PM3 method also gives a good correlation for most of the positions (Fig. 5). The point farthest off the regression line based on BNPA is 2-biphenylene.

In all these correlations with protodetritiation rates, the 9-position of anthracene (9A) is more reactive than predicted from its calculated equilibrium proton affinity. It is also by far the most reactive position in this series. This might indicate a significant change in transition structure. We also sought changes in molecular structure on protonation. Table 3 summarizes structural data at the 6-31G* level for the protonated ring of these PAHs and lists the percentage changes from the neutral hydrocarbon.

When protonation takes place, the two C—C bonds connected to the protonated position are longer because these bonds are now $C_{sp^2}$-$C_{sp^3}$. Of the compounds examined here, only at the anthracene 9-position are both bonds connected to a ring junction. The uniqueness of such positions has been cited previously [22]. Thus, as shown in Table 3, the total percentage change of the two C—C bonds connected to the protonated position in 9A is 16.56%, the largest number among these protonated molecules.

We conclude that calculations at any of these levels should provide excellent predictions of electrophilic aromatic substitution, particularly for normal benzenoid hydrocarbons. The best correlations are given by the HF/6-31G* method. MP2 correction at the 6-31* geometries gives slightly poorer agreement.

*Acknowledgements.* This work was supported in part by NSF grant CHE 95-28273. Dedicated to the memory of Kenichi Fukui whose earliest work included a theoretical study of aromatic substitution.

## References

1. Santodonato J, Howard P, Basu D (1981) In: Lee SD, Grant L (eds) Health and ecological assessment of polynuclear aromatic hydrocarbons. Pathotox, Park Forest S., Ill. p 177
2. Cooke M, Dennis AJ (eds) (1986) Polynuclear aromatic hydrocarbons: chemistry, characterization and carcinogenesis. Battelle Press, Columbus, Ohio

3. Jones PW, Leber P (1979) Polynuclear aromatic hydrocarbons; 3rd international symposium on chemistry and biology-carcinogenesis and mutagenesis. Ann Arbor Science Publishers, Ann Arbor, Mich
4. Laali KK (1996) Chem Rev 96:1873
5. Cavalieri EL, Rogan EG (1985) In: Harvey RG (ed) Polycyclic hydrocarbons and carcinogenesis, ACS symposium series 283. American Chemical Society, Washington, D. C., pp 289
6. Ramakrishna NVS, Cavalieri EL, Rogan EG, Dolnokowski G, Cerny RL, Gross ML, Jeong H, Jankowiak R, Small GJ (1992) J Am Chem Soc 114:1863
7. Rogan EL, Devaresan PD, Cavalieris EL (1991) In: Cook M, Leoning L, Merritt J (eds) Polynuclear aromatic hydrocarbons: measurements, means, and metabolism. Battelle Press, Columbus, Ohio, p 767
8. Streitwieser A Jr (1961) Molecular orbital theory for organic chemists. Wiley, New York
9. Fukui K, Yonezawa T, Shingu H (1952) J Chem Phys 20:722
10. Fukui K, Yonezawa T, Nagata C, Shingu H (1954) J Chem Phys 22:1433
11. Dewar MJS (1952) J Am Chem Soc 74:3357
12. Dewar MJS, Mole T, Warford EWT (1956) J Chem Soc:3581
13. Dewar MJS (1958) Rec Chem Prog 19:1
14. Streitwieser A Jr, Fahey RC (1962) J Org Chem 27:2352
15. Bancroft KCC, Howe GR (1970) J Chem Soc B:1541
16. Streitwieser A Jr, Mowery PC, Jesaitis RG, Lewis A (1970) J Am Chem Soc 92:6529
17. Lias SG, Bartmess JE, Liebman JF, Holmes JL, Levin RD, Mallard WG (1988) J Phys Chem Ref Data 17, Suppl no. 1:1
18. Streitwieser A Jr, Lewis A, Schwager I, Fish RW, Labana S (1970) J Am Chem Soc 92:6525
19. Bancroft KCC, Bott RW, Eaborn C (1972) J Chem Soc Perkin Trans II:95
20. (a) G Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Wong MW, Foresman JB, Robb MA, Head-Gordon M, Replogle ES, Gomperts R, Andres JL, Raghavachari K, Binkley JS, Gonzalez C, Martin RL, Fox DJ, Defrees DJ, Baker J, Stewart JJP, Pople JA (1993) Gaussian 92/DFT, revision G.1. Gaussian, Pittsburgh, Pa; (b) Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong NW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA (1995) Gaussian 94, revision C3. Gaussian, Pittsburgh, Pa
21. Schulman MJ, Peck RC, Disch RL (1989) J Am Chem Soc 111:5675
22. Pointet K, Milliet A, Hoyan S, Renou-Gonnord MF (1997) J Comput Chem 18:629
23. Hunter EP, Lias SG (1998) J Phys Chem Ref Data (in press). See http://webbook.nist.gov/chemistry/
24. Eckert-Maksic M, Fabian WMF, Janoschek R, Maksic ZB (1995) J Mol Struct (Theochem) 338:1
25. Baker R, Eaborn C, Taylor R (1961) J Chem Soc:4927
26. Tamagawa K, Lijima T, Kimura M (1976) J Mol Struct 30:243
27. Kao J, Allinger NL (1977) J Am Chem Soc 99:975
28. Bastiansen Q, Shancke PN (1961) Adv Chem Phys 3:323
29. Kay MI, Okaya Y, Lox DE (1971) Acta Crystallogr Sect B 27:26
30. Schulman JM, Peck RC, Disch RL (1989) J Am Chem Soc 111:5675
31. Mason R (1964) Acta Crystallogr 17:547