Weak Interactions in Crystals: 4,4'-Di(*tert*-butyl)-*N*-*N'*-bipyridinium Diperchlorate—A Biphenyl Analogue with Perpendicular Pyridine Rings

Hans Bock,* Sabine Nick, Christian Näther, and Wolfgang Bensch

Abstract: Oxidation of substituted *N*-aminopyridinium compounds yields bipyridinium salts. After anion exchange $Br^- \rightarrow ClO_4^-$, it was possible to grow single crystals from the 4,4'-di(*tert*-butyl) derivative. The structure determined at 100 K shows a dihedral angle of 84° between the molecular halves connected by a shortened N–N bond of 143 pm in length. This result is contrary to that expected from the isoelectronic correspondence $\rangle C-C\langle \leftrightarrow \rangle\overset{+}{N}-\overset{+}{N}\langle$, which would suggest planarity, as has been observed experimentally both in solid biphenyl, and in tetraalkylhydrazine dications and radical cations. Lattice packing analysis, however, reveals the presence of hydrogen bonds C(H)···O between the phenyl rings and the perchlorate anions. AM1 enthalpy hypersurface calculations for the isoelectronic series $H_5C_5X-YC_5H_5$ ($X-Y = C-C$, ^+N-C, $^+N-N^+$, $^-B-N^+$, ^-B-C, and $^-B-B^-$) predict single-minimum potentials for both the dication $\rangle\overset{+}{N}-\overset{+}{N}\langle$ as well as the dianion $\rangle\overset{-}{B}-\overset{-}{B}\langle$ with the molecular halves twisted perpendicular to each other. In detailed model calculations, counteracting effects of π electron density delocalization vs. H/H repulsion of the *ortho* ring hydrogens adjacent to the central bond seem to dictate the delicate balance of the biphenyl twisting. For further experimental confirmation, the structure of the isosteric molecule 4,4'-di(*tert*-butyl)biphenyl has been determined: in contrast to the unsubstituted π hydrocarbon with a lattice-enforced dihedral angle of 0°, close to the calculated value, the two molecular halves are twisted by 40°—as in biphenyl in the gas phase.

Keywords
biphenyls · bipyridinium salts · conformation · semiempirical calculations · structure elucidation

Introduction

Biphenyl and its derivatives[1] have been extensively investigated: NMR,[2] Raman,[3] UV,[4] and ESR/ENDOR spectroscopy,[5] and cyclovoltammetry[6] provide information on the conformation of the phenyl rings in solution. X-ray and electron diffraction studies have been carried out in the solid as well as in the gaseous phase: The parent compound, biphenyl, exhibits dihedral angles of 42° in the gas phase,[7] 32° in solution,[8] and 25° in the melt,[9] whereas it is completely planar in the crystalline phase[10] above 40 K (Fig. 1).[1] At 40 K, a reversible phase transfer occurs in the solid[11] and the molecular halves twist by 10°.

Molecular mechanics calculations[12] based on appropriate van der Waals potentials C/C, C/H, and H/H reproduce the structures both in the gas phase as well as in the crystal lattice.

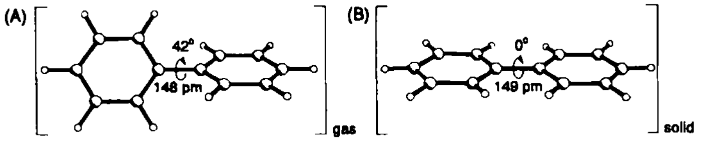

Fig. 1. Conformations of biphenyl in the gas and crystalline (above 40 K) phases.

Quantum chemical model calculations[13] allow the conformation of biphenyl derivatives to be analyzed in terms of competition between π-electron delocalization vs. Coulomb repulsion between the ring *ortho* substituents.[14] The dihedral angle between the two molecular halves depends on intermolecular contacts, as illustrated by the molecular structures of biphenyl (Fig. 1), an impressive example of lattice packing effects.[14, 15]

A search in the Cambridge Structural Database (CSD)[16] for *ortho*-unsubstituted biphenyl derivatives yields 229 entries, of which 19 denote errata and 33 concern disordered crystals. After additional subtraction of repeated structure determinations, 145 compounds remain, which, on inclusion of all independent molecules *n* within the respective units cells, show a characteristic histogram of their ring torsion angles $|\omega|$ with maxima around 0 and 40° (Fig. 2). The histogram demonstrates that biphenyl derivatives with *ortho* hydrogen substituents are mostly either planar or exhibit dihedral angles ω between 25 and 45°. The effect of substituents on the ring torsion is hard to define, because even identically substituted derivatives exhibit different torsional distortions: for instance, 4-hydroxybiphenyl is almost planar in its orthorhombic[17a] and monoclinic[17b] modi-

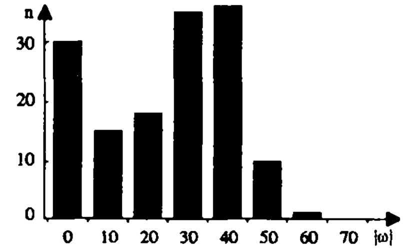

Fig. 2. Distribution of ring torsion angles $|\omega|$ found in *ortho*-unsubstituted biphenyl derivatives.

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fications as well as in its charge-transfer complex with 4,4'-dinitrobiphenyl,[17b] whereas its acetone solvate exhibits a torsion angle of 23°.[17a]

The CC bond length between the phenyl rings is 143–154 pm, with an average length of 149 pm. These values cannot be correlated with the dihedral angles (Fig. 2): for instance, although the length of the CC ring bridge (148 pm) is identical in all three compounds, biphenyl-4,4'-dithiol is completely planar, whereas 4-nitrobiphenyl and bis(4-ethoxycarbonylphenyl) biphenyl-4,4'-dicarboxylate exhibit ring twists of 33 and 48°, respectively.[18]

Starting from the numerous biphenyl derivatives that have been characterized structurally and/or by quantum chemistry (Fig. 2), an obvious question concerns the structural diversity of selected isoelectronic π systems consisting of two six-membered heterocycles (Fig. 3).

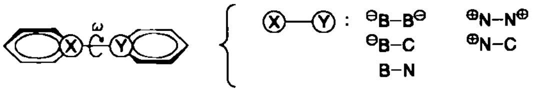
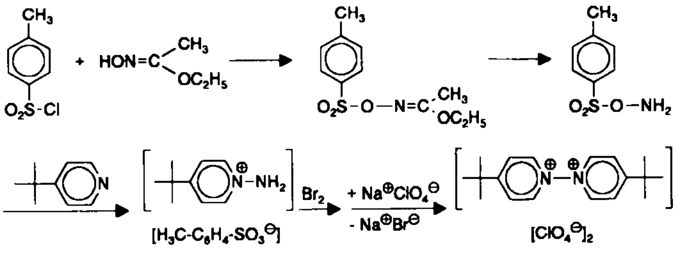


Fig. 3. Isoelectronic π systems.

A CSD search profile yields only six entries on phenylpyridinium[19a] and N-borabenzenepyridinium derivatives.[19b, c] This rather small number of structurally characterized heterobiphenyl analogues highlights the need for further research directed towards the synthesis, crystallization, and structure determination of additional examples. To allow a more rational selection among the manifold of possibilities, dihedral angles between the adjacent rings have been predicted for all compounds (Fig. 3) by AM1 enthalpy hypersurface calculations (Fig. 4).

For a preliminary test whether semiempirical SCF procedures[20] will reliably reproduce the rotational barrier of biphenyl, a one-dimensional AM1 enthalpy of formation hypersurface with total geometry optimization for each twisting step has been calculated (Fig. 4A). The satisfactory result is a double minimum at 42 and 138° with rotational barriers $\Delta\Delta H_f^{\mathrm{AM1}} = 5\ \mathrm{kJ\,mol^{-1}}$ between 42 and 138° and 9 kJ mol^{-1} between 138 and 42°, where the *ortho* hydrogens have to bypass each other. For N-phenylpyridinium cation (Fig. 4B), a less pronounced double minimum results, at 48° and 132° with a rotational barrier of only 2 kJ mol^{-1}. For the N,N'-bipyridinium cation (Fig. 4C) only a single minimum is found, with an unexpectedly high barrier of $\Delta\Delta H_f^{\mathrm{AM1}} = 35\ \mathrm{kJ\,mol^{-1}}$ as the molecule passes through the planar conformation at $\omega = 0°$. The $^-$B–N$^+$ zwitterion (Fig. 4D) exhibits a double minimum at 38 and 142°, comparable to that of biphenyl but with a higher barrier of about 11 kJ mol^{-1} between 38 → 142°, and only 4 kJ mol^{-1} for the torsion 142 → 38° through planarity. For the B-phenylborabenzene anion (Fig. 4E), a rather smooth double minimum is predicted with a rotational barrier with $\Delta\omega$ analogous to that for the phenyl-substituted $^+$N–C cation (Fig. 4B). For the B,B'-diborabenzene dianion, a single minimum is calculated in close analogy to the bipyridinium dication (Fig. 4C). Rotation through the planar conformation should require only 10 kJ mol^{-1}. All of the above predictions, which can be compared to known experimental data,[19a, b] confirm the reliability of the AM1 calculations.[20] Both the N,N'-bipyridinium dication and the B,B'-diborabenzene dianion should possess molecular skeletons with the two six-membered rings approximately perpendicular to each other.

Following the above reasoning, 4,4'-di(*tert*-butyl)-N,N'-bipyridinium diperchlorate has been selected as a model compound and synthesized by the modified four-step procedure shown in Scheme 1 (see Experimental Section).[21] Following anion exchange Br$^-$ → ClO$_4^-$ (see Experimental Section), single crystals suitable for crystal structure determination could be grown from an acetonitrile/methanol solution.



Scheme 1. Synthesis of 4,4'-di(*tert*-butyl)-N,N'-bipyridinium diperchlorate.

To further test the hypothesis that "spreading the crystal lattice", that is, reducing the density by introducing bulky *tert*-butyl substituents, allows increased phenyl-ring dynamics, the crystal structure of the isosteric 4,4'-di(*tert*-butyl)-biphenyl has been determined, for which the AM1 calculations predict a dihedral angle of 42° (Fig. 4A).

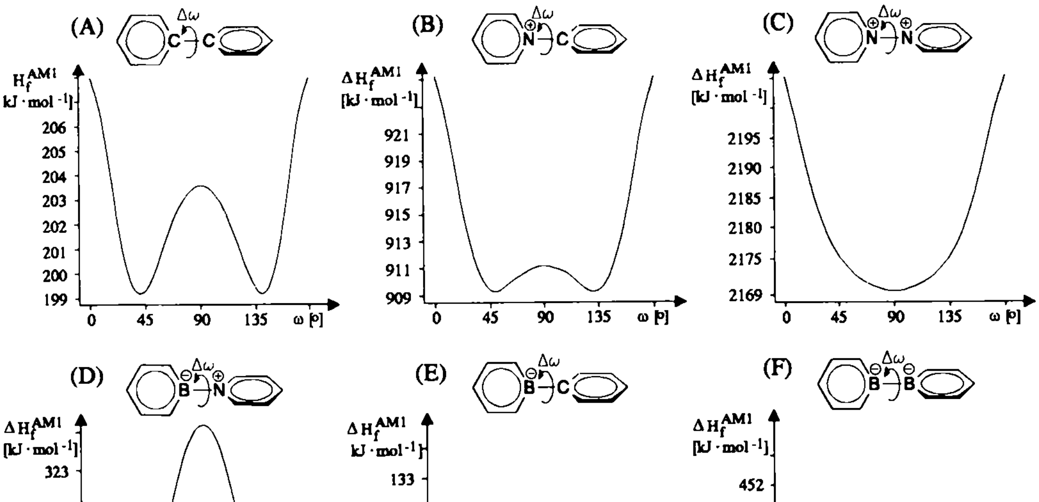


Fig. 4. AM1 rotational barriers $\Delta H_f^{\mathrm{AM1}}$ [kJ mol^{-1}] for (A) biphenyl, (B) N-phenylpyridinium cation, (C) N,N'-bipyridinium dication, (D) N-borabenzenepyridinium zwitterion, (E) B-phenylborabenzene anion, and (F) B,B'-diborabenzene dianion.

Experimental Section

Ethyl *O-p*-Tosylacetohydroximate [21b]: Triethylamine (24.8 mL, 178 mmol) was added to ethyl acetohydroximate (18 g, 174 mmol) in DMF (120 mL) at room temperature. The reaction mixture was cooled to 0 °C, and tosyl chloride (32.2 g, 174 mmol) was added within 10 min. The yellow solution was stirred for 2 h at 20 °C, triethylamine hydrochloride filtered off, the solvent partly removed at 1 mbar, and the remaining solution poured into ice-water (1.2 L). The white precipitate was dried over KOH to yield 32.6 g (73 %) of the product with m.p. 64–67° (ref. [21b]: 70–71°).

***O-p*-Tosylhydroxylamine** [21c]: To the ethyl ester (15 g, 58 mmol) was added 60 % $HClO_4$ (50 mL, 283 mmol), and the solution was stirred for 5 min until gas evolution had ceased. After the reaction mixture had been cooled to 0 °C, ice-water was added to give a total volume of 250 mL. The white precipitate was filtered off and immediately dissolved in 90 mL of a 1 M $NaHCO_3$ solution. When CO_2 was no longer eliminated, the solid was filtered off again and immediately dispersed in ice-water.

***N*-Amino-4-*tert*-butylpyridinium *p*-Tosylate** [21a]: The aqueous dispersion of *O-p*-tosylhydroxylamine was repeatedly extracted with a total of 130 mL CH_2Cl_2. 4-*tert*-Butylpyridine (8.57 mL, 58 mmol) was added, and the mixture stirred at 20 °C for 2 h. After addition of the fivefold volume of diethyl ether, 5.65 g (30 %) of the white tosylate with a m.p. of 118–119 °C (ref. [21a]: 118–120 °C) was isolated.

4,4′-Di(*tert*-butyl)-*N*,*N*′-bipyridinium Dibromide [21a]: The tosylate was dissolved in water (100 mL) and bromine-saturated water (285 mL) added. A red oil separated from the resulting red reaction mixture and was decanted. Surplus bromine was removed from the oil in vacuo at 20 °C. Acetone (130 mL) was added, and the mixture was refluxed for 30 min. The precipitate was filtered off and recrystallized from diethyl ether, yielding 700 mg (9 %) of white needles with m.p. 311–312 (ref. [21a] = 310 °C). ^1H NMR ($[D_6]$DMSO): $\delta = 1.47$ (s, 18 H), 8.7, 9.7 (dd, 8 H, AA′BB′).

4,4′-Di(*tert*-butyl)-*N*,*N*′-bipyridinium Diperchlorate: The bromide was dispersed in anhydrous acetonitrile and dissolved by adding methanol. After a solution of $NaClO_4$ in acetonitrile had been added, crystals began to grow with a m.p. of 325 °C. ^1H NMR ($[D_6]$DMSO): $\delta = 1.47$ (s, 18 H), 8.6, 9.6 (dd, 8 H, AA′BB′). IR: $\tilde{\nu} = 3100-2900$ (s, C–H), 1620 (s, C=C), 1500 (s, C=N), 1330 and 1370 cm^{-1} (m, $C(CH_3)_3$).

Crystal Structure of 4,4′-Di(*tert*-butyl)-*N*,*N*′-bipyridinium Diperchlorate: $C_{18}H_{26}N_2 \cdot 2ClO_4^-$, colorless prisms, crystal dimensions: $0.4 \times 0.3 \times 0.3$ mm^3, $M_r = 469.32$, $a = 611.9(2)$, $b = 1298.3(5)$, $c = 1435.7(6)$ pm, $\alpha = 102.29(3)$, $\beta = 98.10(3)$, $\gamma = 91.30(3)°$, $V = 11101.67 \times 10^6$ pm^3, ($T = 100 \pm 0.5$ K), $\rho_{calcd} = 1.487$ g cm^{-3}, triclinic, $P\bar{1}$ (No. 2), $Z = 2$, $Mo_{K\alpha}$ radiation, $\lambda = 71.073$ pm, $\mu = 0.034$ cm^{-1}. STOE-AED-II four-circle diffractometer, 5562 reflections measured within $3 \leq 2\theta \leq 48°$, of which 2548 are independent with $I > 1.5\sigma(I)$. Structure solution by direct methods and using difference Fourier technique (SHELXTL PLUS). $R = 0.0576$, $R_w = 0.0407$ for 344 parameters, $w = 1/\sigma^2(F) + 0.00015F^2$, GOOF = 1.6845, shift/error ≤ 0.001, residual electron density 0.44/−0.50 e Å^{-3}. C, N, O, and Cl positions have been refined with anisotropic and the H centers with isotropic displacement parameters.

Crystal Structure 4,4′-Di(*tert*-butyl)biphenyl: The compound (Fluka) crystallizes on slow cooling of a hot saturated methanol/water solution as transparent prisms, which are suitable for crystal structure determination. Crystal dimensions: $0.4 \times 0.3 \times 0.2$ mm^3. $C_{20}H_{26}$, $M_r = 266.41$, $a = 823.2(4)$, $b = 1015.9(5)$, $c = 1180.7(5)$ pm, $\alpha = 66.71(5)$, $\beta = 84.01(3)$, $\gamma = 71.33(4)°$, $V = 858.9(7) \times 10^6$ pm^3 ($T = 293$ K), $\rho_{calcd} = 1.03$ g cm^{-3}, triclinic, $P\bar{1}$ (No. 2), $Z = 2$, $Cu_{K\alpha}$ radiation, $\lambda = 154.18$ pm, $\mu = 0.0423$ cm^{-1}. Enraf-Nonius CAD-4 diffractometer, 3520 reflections within $8 \leq 2\theta \leq 100°$, of which 1760 independent with $I > 1.5\sigma(I)$. Structure solution by direct methods using difference Fourier technique (SHELXTL PLUS). Refinement vs. F^2 (SHELXTL-93). $R1 = 0.0701$ for 1530 $F_0 > 4\sigma(F_0)$, $wR2 = 0.2001$ for 200 parameters and 1760 reflexions, $R_{int} = 0.0332$. $w = 1/[(\sigma^2(F_o^2) + 0.1082P)^2 + 0.24P]$, GOOF = 1.055, shift/error ≤ 0.001, extinction correction, residual electron density 0.15/−0.11 e Å^{-3}. C positions are refined with anisotropic and H positions, after ideal geometrical positioning, with isotropic displacement parameters according to the riding model. The *tert*-butyl groups are disordered in two orientations and, therefore, were refined using a split model and identical displacement parameters for each opposite split positions.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59111.

AM1 Calculations were performed using the AMPAC/SCAMP program package (M. J. S. Dewar [20], modified by Dr. T. Clark, University of Erlangen) on the IBM RISC 6000-320 of our group. Starting from the structural coordinates, the rotational barriers were approximated in 10° steps with each total geometry optimization. For additional discussions of NN bonds see, for example, ref. [22].

Results

Crystal Structure of 4,4′-Di(*tert*-butyl)-*N*,*N*′-bipyridinium Diperchlorate: In the crystal lattice, the dications and the anions are arranged in segregated stacks along the crystallographic *a* axis (Fig. 5 A). The pyridinium rings and the perchlorate anions are connected by intermolecular hydrogen bonds C–H···($^-OClO_3$) (Fig. 5 B and Table 1).

The hydrogen bonds C-H···($^-OClO_3$) from the bipyridinium dications to the two different perchlorate anions (Fig. 5 and Table 1) are rather short. According to a search in CSD,

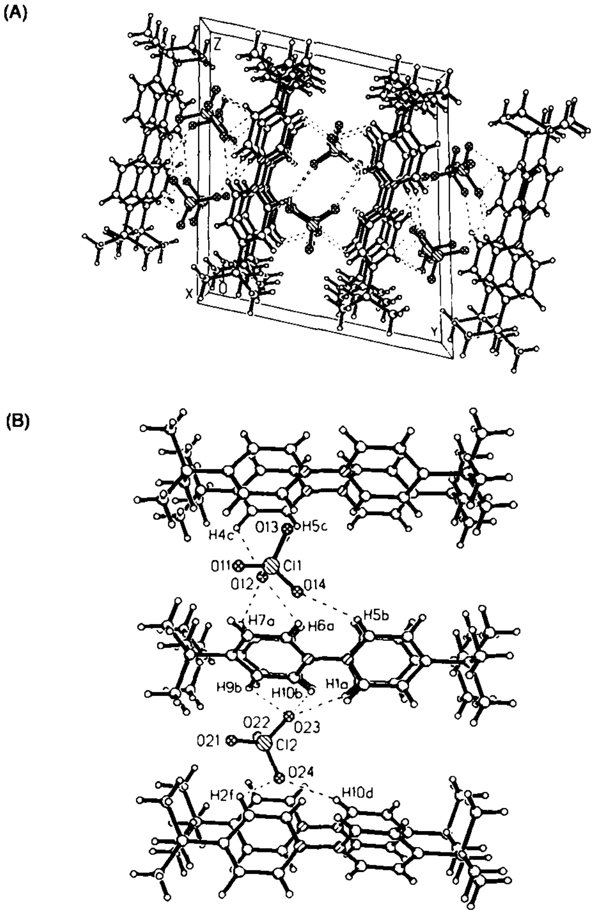


Fig. 5. Single crystal structure of 4,4′-di(*tert*-butyl)-*N*,*N*′-bipyridinium perchlorate at 100 K (triclinic, space group $P\bar{1}$, $Z = 2$): (A) Unit cell viewed along the crystallographic *a* axis and (B) details of hydrogen bonds C–H···($^-OClO_3$) between a perchlorate anion and four dications (cf. Table 1).

Table 1. Hydrogen bonds C–H···O in 4,4-di(*tert*-butyl)-*N*,*N*′-bipyridinium diperchlorate at 100 K: distances *d*(C(H)···O) and *d*(O···H) [pm], and angles ∢(C–H···O) [°] (for numbering, see Fig. 5).

C–H···($^-OClO_3$)	*d*(C(H)···O)	∢(C–H···O)	*d*(O···H)
H 6a O12	314	117	259
H 7a O12	308	124	245
H 5c O12	321	124	257
H 5c O13	322	132	250
H 5b O14	324	140	245
H 4c O12	326	124	256
H 10b O23	313	118	258
H 9b O23	317	126	255
H 2f O24	320	119	265
H 1a O23	321	156	239
H 10d O24	325	153	238

the shortest bond so far[23] reported is for the double adduct of trinitromethane to dioxane $(O_2N)_3CH\cdots O(CH_2CH_2)_2O\cdots HC(NO_2)_3$ with distances $C\cdots O$ of only 294 pm.[23a] The shortest hydrogen bond in the bipyridinium diperchlorate exhibits a $C\cdots O$ distance of 308 pm (Table 1), which, according to SCF calculations,[23–25] should correspond to energy contributions of 2–4 $kJ\,mol^{-1}$. Multiple hydrogen bonds[25] such as between the dications and the interspersed perchlorate counter anions in the bipyridinium diperchlorate (Fig. 5, Table 1), should promote the twisting of the almost perpendicular pyridinium rings (Fig. 6: $\omega = 84°$).

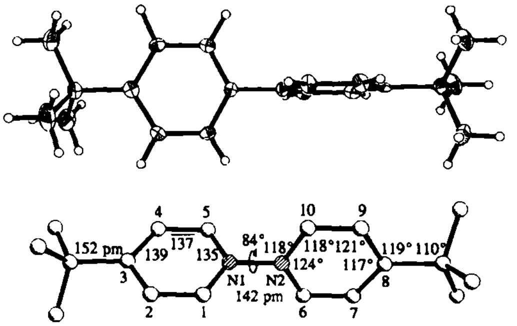


Fig. 6. Crystal structure of 4,4'-di(*tert*-butyl)-*N,N'*-bipyridinium diperchlorate at 100 K (ellipsoids at the 50% probability level).

The structure of 4,4'-di(*tert*-butyl)-*N,N'*-bipyridinium diperchlorate, which was determined at 100 K (Fig. 6, Table 2), shows a torsion angle of 84° between the two positively charged six-membered rings—in nearly perfect agreement with the energetically most favored conformation predicted by AM 1 calculations (Fig. 4C).

Table 2. Crystal structure of 4,4'-di(*tert*-butyl)-*N,N'*-bipyridinium dication at 100 K: selected bond lengths [pm] and angles [°] (for numbering, see Fig. 6).

N1 –N2	141.6(2)	N1-N2-C6	118.3(2)
N1 –C1	134.2(2)	N1-N2-C10	117.9(2)
N1 –C5	134.5(2)	C6-C7-C8	121.5(2)
C1 –C2	135.7(2)	C7-C8-C9	117.3(2)
C2 –C3	139.9(2)	C9-C10-N2	118.4(2)
C3 –C4	138.9(2)	C8-C15-C16	111.8(2)
C4 –C5	137.7(2)	C8-C15-C17	109.8(2)
C3 –C11	152.2(2)	C8-C15-C18	107.0(2)
C11–C12	152.3(2)	C6-N2-C10	123.8(2)
C11–C13	153.5(2)		
C11–C14	153.7(2)	C1-N1-N2-C6	84.7(3)

The following remarkable structural features of the molecule shown in Figure 6 are worth pointing out: The N–N bond (142 pm) is 7 pm shorter than the $C_{ring}-C_{ring}$ bond in biphenyl (Fig. 1), whereas the ring $\overset{+}{N}$=C and C=C bond lengths are within the usual range.[26] The *ipso* angle of 124° at the pyridinium center is widened by 7° relative to pyridine;[27] this indicates an acceptor-type substitution.[1, 27b] The other *ipso* angles at C3 and C8 (Fig. 6) are, as expected, reduced from 120° to 117° by the substituent effect of the $(H_3C)_3C$ donor.[1, 27b]

Discussion

The energetic hierarchy of structural perturbations—bond lengths > bond angle changes ≫ conformational twist differences—is well established.[28] For π systems with two connected six-membered rings, the dihedral angle between their π planes must be the most sensitive structural probe both for electronic as well as for lattice effects.

AM 1 Calculations: The AM 1 enthalpy of formation hypersurfaces for the 4,4'-di(*tert*-butyl) derivatives of biphenyl and the *N,N'*-bipyridinium dication are comparable to those for their unsubstituted parent systems (Fig. 4A and C),[1b] and the discussion of the different structures in terms of dominant counteracting π delocalization versus *ortho* H/H repulsion can therefore be based on the latter.

The π delocalization is assessed by the dependence of the π bond order $p^{\pi\pi}$ on the dihedral angle ω (Fig. 7). As expected, the π bond order in biphenyl, *N*-phenylpyridinium cation, *N*-borabenzenepyridinium betaine, and *B*-phenylborabenzene an-

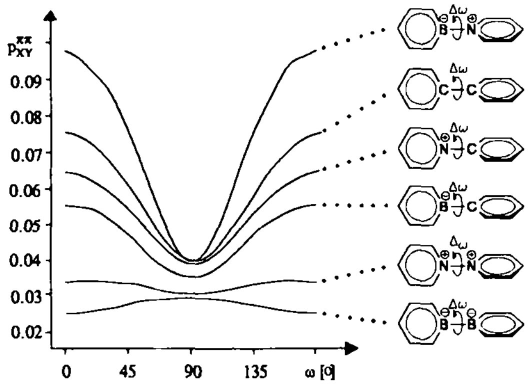


Fig. 7. Dependence of the π bond order $p^{\pi\pi}$ on the dihedral angle ω.

ion is highest in the planar conformations at 0 and 180°. For the $^+N-N^+$ central bond in *N,N'*-bipyridinium dication, surprisingly, a rather small and rotationally independent π electron density is predicted.[30] For the $^-B-B^-$ bond in diborabenzene dianion a shallow minimum at 0 and 180° is calculated.

The weak ring π/π interaction in the *N,N*-bipyridinium dication can be further substantiated by discussing the conformational dependence of the π electron density in terms of the squared coefficients $c^2_{12,\pi}$ of the highest occupied orbital (Fig. 8, cf. Fig. 4). In planar biphenyl ($\omega = 0°$), the relatively high squared π coefficients of the bridging C centers increase on twisting ($c^2_{12,\pi}(90°)$ in Fig. 8). In *N*-phenylpyridinium cation, most of the π density is located in the phenyl ring, and a nodal plane develops on twisting from 0 to 90° and removes all π contributions from the pyridinium ring. In the planar *N,N'*-bipyridinium dication, a perpendicular nodal plane contains the long molecular axis, and, due to zero coefficients at the N centers, there is no π interaction between the two rings at either $\omega = 0$ or 90°. In the borabenzenepyridinium betaine and in the *B*-phenylborabenzene anion, the π electron density should be predominantly located in the boron six-membered ring at $\omega = 0°$. At $\omega = 90°$ all of it will be located in the boron six-membered ring. In the hypothetical diborabenzene dianion, the highest π density is at the 4-position and relatively little in the central B–B bond at $\omega = 0°$. On twisting to $\omega = 90°$ a π-charge localization over both rings is calculated by the AM 1 procedure.

The Coulombic repulsion between the hydrogens adjacent to the central $^+N-N^+$ bond can be approximated by partitioning of the total energy with respect to invidual centers.[20] As expected, the sum of the four H/H positive enthalpy components de-

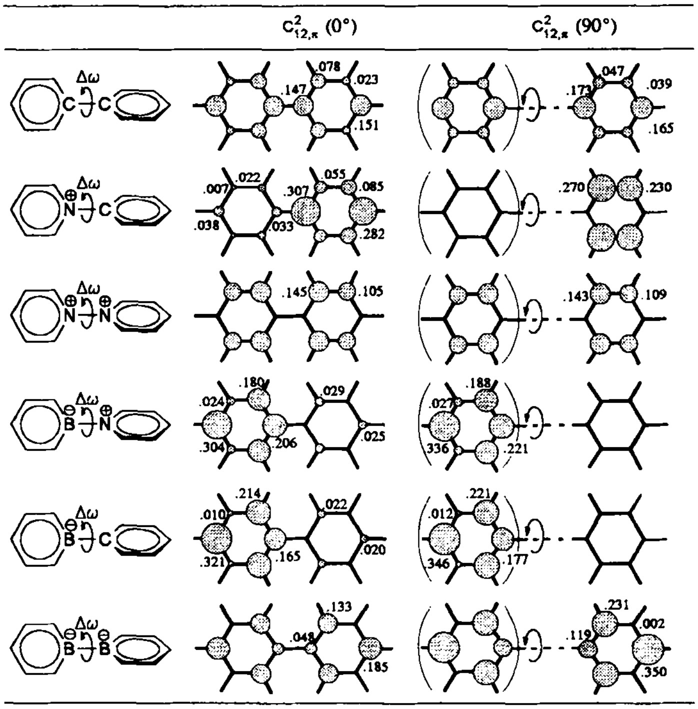


Fig. 8. Conformational dependence of the π electron density in terms of the squared coefficients $c^2_{12,\pi}$ of the highest occupied orbital.

pends strongly on the H···H distances and counteracts the effect of π delocalization (Fig. 7). For all biphenyl derivatives considered (Fig. 9), the H/H repulsion increases towards planarity and with decreasing central X–Y bond length. For the N,N'-bipyridinium dication, which has the shortest X–Y bond ($d(^+N-N^+) \approx 140$ pm), the repulsion reaches its highest value of 83 kJ mol^{-1}. With increasing bond lengths—144 pm in the phenylpyridinium cation, 146 pm in biphenyl, and 150 pm in N-borabenzenepyridinium betaine—the repulsion enthalpy decreases from 51 to 28 and 27 kJ mol^{-1}, respectively. The two negatively charged derivatives B-phenylborabenzene anion and B,B'-diborabenzene dianion, with ^-B-C and $^-B-B^-$ bond lengths of 155 and 160 pm, approach rather shallow minima of 11 and 3 kJ mol^{-1}, respectively.

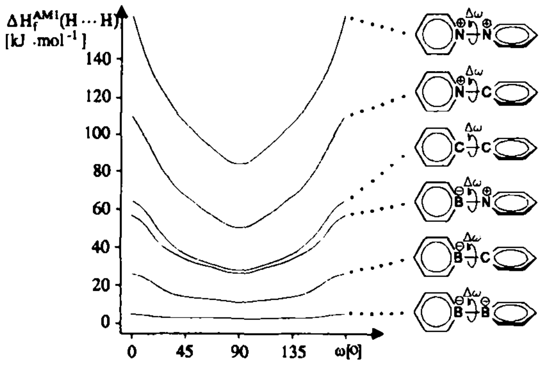


Fig. 9. Calculated dependence of the H/H repulsion on ω.

A superposition of the two counteracting effects, namely, π delocalization (Fig. 7) and H/H repulsion (Fig. 9), which are assumed to determine the twist of the connected six-membered rings, indeed reflects the potential curves of the six molecules and molecular ions selected. Accordingly, the rotational barrier of the title compound, the N,N'-bipyridinium dication should be determined predominantly by the Coulomb repulsion between the four positively charged hydrogens surrounding the rather short N–N bond. In biphenyl, in the N-phenylpyridinium cation, and in the phenylborabenzene anion, the stabilization due to π charge delocalization plays a more important role.

In borabenzenepyridinium betaine ($H_5C_5\overset{-}{B}-\overset{+}{N}C_5H_5$), the planar conformation at dihedral angles of 0 or 180° is favored by the high π bond orders (Fig. 7), which enforce the considerable rotational barrier at ω = 90°. Also in B,B'-diborabenzene dianion with its BB bond of 160 pm predicted by AM 1 calculations, the π delocalization of the two negative charges is the essential conformational driving force, relative to which the comparatively small H/H Coulomb repulsion between the less polarized *ortho* hydrogens is negligible.

The differently polarized $C^{\delta-}-H^{\delta+}$ bonds can clearly be recognized also in the total charges at the various centers calculated by AM 1, for instance, in the calculations (Fig. 10) based on the structural coordinates of the two compounds characterized here. The prediction of a considerable polarization of the H–C ring bonds adjacent to $^+N-N^+$, which is less pronounced in the corresponding bonds of 4,4'-di(*tert*-butyl)biphenyl—even if this effect is exaggerated by the AM 1 procedure[20]—would be worth investigating further.

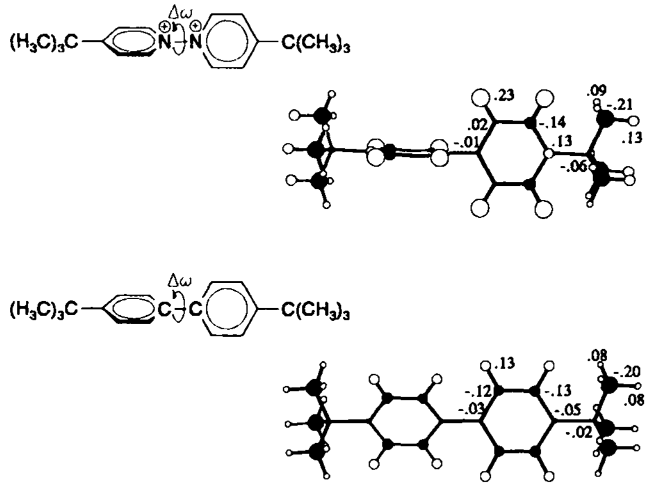


Fig. 10. Total charges at the various centers in the 4,4'-di(*tert*-butyl)-N,N'-bipyridinium dication and in 4,4'-di(*tert*-butyl)biphenyl calculated by AM 1.

The Crystal Structure of 4,4'-Di(*tert*-butyl)biphenyl: In conclusion, the structural comparison between the $^+N-N^+$ dication and the isoelectronic 4,4'-di(*tert*-butyl)-substituted neutral C–C derivative is presented.

4,4'-Di(*tert*-butyl)biphenyl crystallizes in layers (Fig. 11 A) with a dense lattice packing, achieved by filling the spaces above the phenyl rings with *tert*-butyl substituents (Fig. 11 B). The calculated lattice density of 1.03 g cm^{-3}, based on a structure determined at 293 K, is considerably lower than that measured for 4,4'-dimethyl-biphenyl (D(293 K) = 1.12 g cm^{-3}[29]) and yet lower than that of biphenyl (D(293 K) = 1.18 g cm^{-3}[10d]). These values, measured at comparable temperatures, show that the density decreases[15] with increasing bulk of the 4,4'-substituents ($H < CH_3 < C(CH_3)_3$). This suggests that the favorable lattice packing of planar biphenyl with optimum π delocalization is no longer found in the 4,4'-dialkyl derivatives and espe-

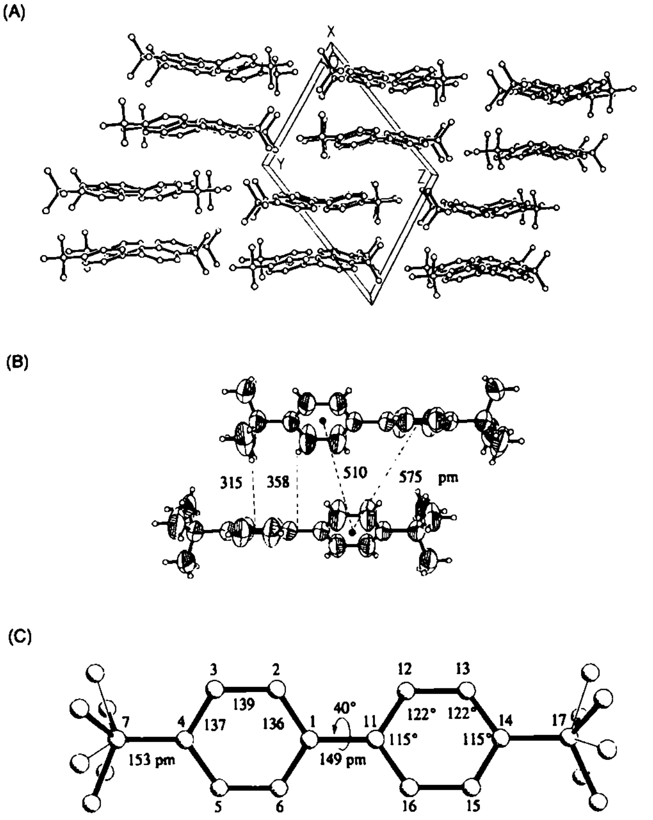


Fig. 11. Single crystal structure of 4,4'-di(*tert*-butyl)biphenyl at room temperature (triclinic, space group $P\bar{1}$, $Z = 2$): (A) Unit cell viewed along the crystallographic *a* axis (split positions of the *tert*-butyl groups omitted), (B) pair of molecules (thermal ellipsoids of the disordered *tert*-butyl groups at the 50% probability level) with shortest distances for $CH\cdots C_{ring}$ contacts as well as those between the ring centroids, and (C) angles and libration-corrected (see Experimental Section) bond lengths.

cially not in the 4,4'-di(*tert*-butyl) case—here the hydrogen-rich substituents decrease the density and, in addition, spread the layers owing to less favorable packing. On the other hand, different lattice interactions can be recognized (Fig. 11 B): The distance of only 510 pm between the centroids of the six-membered rings would, for instance, allow "herringbone" and "shifted ring" type stabilization, recognized ten years ago in the structures of phenyl-containing proteins[30] and, more recently, calculated for benzene dimers, which were investigated experimentally by laser hole-burning in the gas phase.[31] In addition, the relatively short distances separating methyl groups and the ring centroid of the closest phenyl group (Fig. 11 B: 315 pm) should be noted. The minimum value that has been observed is 288 pm, which indicates the onset of interpenetration with respect to the sum of the van der Waals radii ($r_p + r_H = 170 + 120 = 290$ pm).[32]

As also expected, the molecular structure of 4,4'-di(*tert*-butyl)biphenyl (Fig. 11 C) exhibits twisted phenyl rings, with the experimentally determined value of 40° closely resembling the calculated AM 1 value of 42°. The central C–C bond length of 149 pm is consistent with the plot of partitioned enthalpy differences $\Delta H_f^{AM1}(H\cdots H)$ for H/H repulsion (Fig. 9). The structure determined for the C–C analogue of the 4,4'-di(*tert*-butyl)-*N*,*N*'-bipyridinium dication provides all necessary information as a second calibration point for the extensive AM 1 calculations (Fig. 7–9) within the isoelectronic series of compounds $H_4C_5X{-}YC_5H_4$, where X–Y = $^-$B–N$^+$, C–C, $^+$N–C, $^-$B–C, $^+$N–N$^+$, and $^-$B–B$^-$ (Fig. 3).

Retrospective and Perspective

The molecular conformations of biphenyl and its isoelectronic analogues have been experimentally determined and reproduced by extensive semiempirical AM 1 calculations. The enthalpy hypersurfaces for varying dihedral angles predict a double-minimum potential for biphenyl, *N*-borabenzenepyridinium betaine, *N*-phenylpyridinium cation, and *B*-phenylborabenzene anion. In contrast, for *B*,*B*-diborabenzene dianion and the *N*,*N*'-bipyridinium dication only a single-minimum potential results, which suggests a 90° twist angle between the molecular halves. All of the AM 1 predictions, which can be tested experimentally, are confirmed, including the structure of 4,4'-di(*tert*-butyl)biphenyl, which exhibits a dihedral angle of 40° (vs. 42° calculated). The title compound, 4,4'-di(*tert*-butyl)-*N*,*N*'-bipyridinium diperchlorate, of hitherto unknown structure, also adopts the predicted conformation with both molecular halves perpendicular to each other. Generally, the different shape of the potential curves calculated can be traced to the counteracting effects of Coulomb repulsion between the *ortho* ring hydrogens adjacent to the central bond and the π/π interaction between the two unsaturated six-membered rings connected by it.

The scarcity of structurally characterized molecules and molecular ions isoelectronic to biphenyl should stimulate research directed towards both the synthesis and single-crystal structure determination of further novel derivatives. The conformation of the as yet unknown *B*,*B*'-diborabenzene dianion would be of particular interest, for which a 90° twist angle is predicted, analogous to the bipyridinium dication reported above.

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