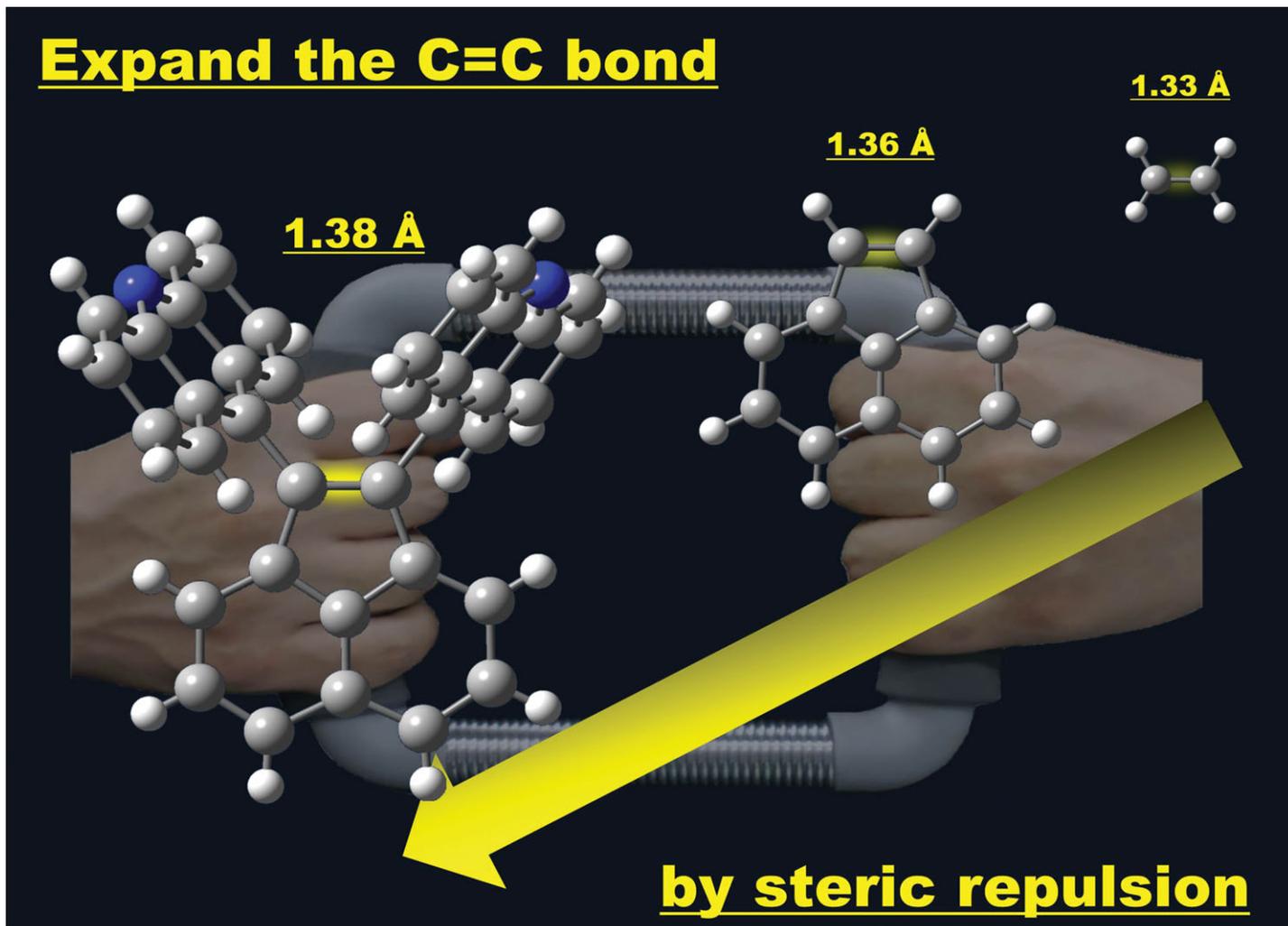


Expand the C=C bond

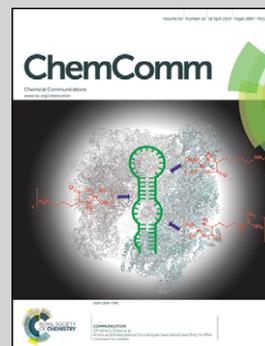


Showcasing research of Dr Takashi Takeda *et al.* from Prof. Takanori Suzuki's Laboratory, Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido, Japan.

Preparation and structure of acenaphthylene-1,2-diyldi(9-acridine) derivatives with a long C=C bond

Investigation of covalent bonds with unusual parameters should provide information on the nature of covalent bonds. Long C=C bond while maintaining its sp^2 hybridization and bond order is now available by rational molecular design. Steric effect around the C=C bond contributes to elongate the bond.

As featured in:



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Preparation and structure of acenaphthylene-1,2-diyl(9-acridine) derivatives with a long C=C bond†

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Takashi Takeda,^{*a} Yasuto Uchimura,^b Hidetoshi Kawai,^c Ryo Katoono,^b
Kenshu Fujiwara^b and Takanori Suzuki^{*b}

Due to purely steric effects of acridine units, acenaphthylene-1,2-diyl(9-acridine) has a long C=C bond [1.3789(19) Å] while maintaining its sp² hybridized nature and bond order.

It is important to achieve a better understanding of the nature of covalent bonds because covalent bonding is a fundamental concept in chemistry. The comparison of “normal” bonds to bonds with unusual parameters, such as bond lengths or angles, is an important method for gaining insight into covalent bonds. Many studies have been based on this idea,¹ and especially on the C–C single bond, which is one of the most common covalent bonds in organic compounds. Long C–C bonds have been found in hexaphenylethane derivatives,² in which steric repulsion between six aryl groups around the C–C bond causes bond elongation.³ Extreme examples have been found in derivatives of tetraarylbenzocyclobutene^{2b,c} and tetraarylpyracene,^{2d-f} in which the C–C bond is longer than 1.7 Å (standard value: 1.54 Å).

Strained C=C bonds have been used as highly reactive intermediates in synthetic chemistry.⁴ There are several types of strained C=C bonds,^{5,6} including C=C bonds with a twisted structure⁶ or pyramidalized carbons, an unusual C=C–C bond angle, and a long or short bond length (Fig. 1).

As in the case of highly expanded C–C bonds, the elongation of a C=C double bond would be induced by geometrical strain. However, there have been fewer successful studies on the elongation of a

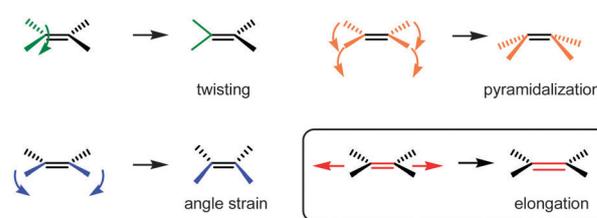


Fig. 1 Types of strain in C=C bonds.

C=C double bond while maintaining its sp²-hybridized nature and bond order. The major concern is that the π-bond order of the C=C bond is easily reduced just by the attachment of electron-donating/-accepting substituents or π-systems. Therefore, in many cases, the observed bond elongation resulted from the reduced bond order but not from geometrical strain. Furthermore, it has been reported that the C=C bond can be stretched by the introduction of cationic coordinating substituents adjacent to the C=C bond: *e.g.*, the coordination of cationic transition metals to 1,2-diaminoethylene causes C=C bond elongation.⁷ However, this method also decreases the π-bond order because of the formation of carbon–metal bonds. To investigate the relationship between the bond length and the nature of the C=C double bond, we must exclude such “impure” C=C double bonds with the reduced bond order from the following discussion.

Based on studies on the long C–C single bonds in hexaphenylethane derivatives, we expected that a steric effect around two carbon nuclei could be a good way to expand a C=C double bond without changing its π-bond order. Since there can be fewer possible substituents around a C=C bond than around a C–C bond, expansion of a C=C bond by steric repulsion should give a smaller change in length. Thus, precise determination with small experimental errors is essential. Hitherto, there have been few attempts to elongate a C=C bond using this approach. It has been reported that, even with the attachment of two bulky groups, the C=C bond length in (*Z*)-1,2-di(1-adamantyl)ethylene⁸ [1.34(1) Å] is almost the same as the standard C=C bond length (1.33 Å),^{9,10} and the value was determined only with a large estimated standard deviation (0.01 Å). Although octachlorobifluorene has a long C=C

^a Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-8577, Japan. E-mail: takeda@tagen.tohoku.ac.jp; Fax: +81-22-217-5654; Tel: +81-22-217-5655

^b Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan. E-mail: tak@mail.sci.hokudai.ac.jp; Fax: +81-11-706-2714; Tel: +81-11-706-2714

^c Department of Chemistry, Faculty of Science, Tokyo University of Science, Shinjuku, Tokyo 162-8601, Japan

† Electronic supplementary information (ESI) available: Experimental procedures and characterization data, details of X-ray single-crystal structure analyses, ORTEP drawings of 1–6, and Cartesian coordinates for the optimized structures of 1–6, acenaphthylene, acenaphthylene-5,6-diyl(9-acridine) and acefluoranthylene. CCDC 975883–975890. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc49573f



bond [1.392(4) Å], its elongation is not mainly due to steric repulsion but accompanied by bond twisting (twist angle of 66°) to reduce the π -bond order.^{6b} However, we envisaged that selection of the rigid double-bond scaffold and bulky substituents could still give a chance to expand a C=C double bond while maintaining its sp^2 -hybridized nature and bond order.

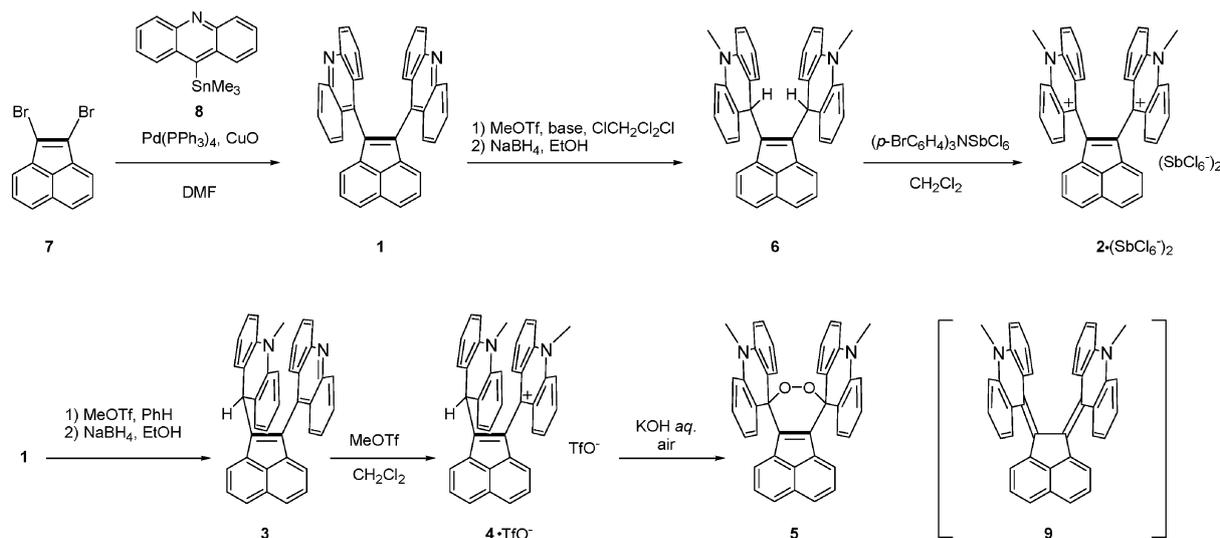
As a rational molecular design to attain severe steric repulsion around the C=C bond, we selected 1,2-disubstituted acenaphthylenes. Due to the rigid molecular framework of acenaphthylenes, the substituents at the C₁ and C₂ positions should be placed in close proximity, thus generating enough repulsion to expand the C=C bond. Another merit of the use of the acenaphthylene-1,2-diyl skeleton is that the C₁=C₂ bond in a five-membered ring would be expanded before the substituents are attached at the C₁ and C₂ positions due to the “clamping” effect, which makes it easy for the bond length to be affected by bulky substituents because the prestrained bond is more susceptible to steric perturbation.¹¹

The C₁=C₂ bond length (d_1) of parent acenaphthylene estimated by DFT calculations (B3LYP/6-31G*) is 1.364 Å.¹² The expansion comes with the “clamping” effect but not due to formal conjugation with the naphthalene subunit. The isolation of the C₁=C₂ bond from conjugation is indicated by the lack of closed-shell resonance structures of acenaphthylene with a C₁-C₂ single bond. The bond length of C_{1(or 2)}-C_{8a(or 2a)} of acenaphthylene (d_2 : 1.473 Å, DFT) is almost the same as that of the standard Csp²-Csp² single bond (1.478 Å for an unconjugated C=C-C=C bond),¹⁰ which supports the above idea. Experimentally determined d_1 and d_2 values are 1.351(3) and 1.483(3) Å in acenaphthylene-5,6-diylidene(9-acridine),^{2d} and 1.362(3) and 1.488(3)-1.491(2) Å in acefluoranthylene,¹⁴ respectively, which is close to the calculated values (1.361 and 1.470 Å for the former and 1.369 and 1.485 Å for the latter, respectively). Thus, the C₁=C₂ bond in acenaphthylenes can be considered to be a prestrained but “pure” C=C bond, whose geometries are close to those estimated by DFT calculation.¹² Herein, we sought to expand the prestrained C₁=C₂ bond of acenaphthylene by applying purely

strain effects to observe the elongated C=C bond while maintaining its sp^2 -hybridized nature and order.

To achieve sufficient steric repulsion around the C=C bond to expand the bond, we expected that the introduction of large planar groups would be effective. Because of nearly perpendicular arrangement of the planar groups to the π -plane of the C=C bond, the decrease in steric repulsion by skewing of the framework or the pyramidalization of Csp²-carbons is inefficient. Thus, steric repulsion could be relieved only by bond expansion and not by other modes of deformation. Even when we choose planar π -systems as substituents on C₁ and C₂, their conjugating effects would be negligible due to their twisted arrangement toward the C₁=C₂ bond. Therefore, we designed acenaphthylene-1,2-diylidene(9-acridine) **1** as a promising target for elongating the C=C bond without changing its sp^2 -hybridized nature and bond order. The acridine substituent in **1** is more feasible than a hydrocarbon counterpart due to its modifiability into several derivatives **2-6**, the structures of which offer useful information for discussing the steric/electronic effects on bond elongation in **1**. The details will be described below.

Acenaphthylene-1,2-diylideneacridine **1** and its derivatives **2-6** were prepared as summarized in Scheme 1. The CuO-promoted Stille coupling¹⁵ of 1,2-dibromoacenaphthylene **7**¹⁶ with 9-(trimethylstannyl)acridine **8**¹⁷ gave diacridine **1** as a sparingly soluble yellow solid. Dimethylation by MeOTf in CH₂Cl₂ gave dication salt **2**·(TfO⁻)₂. To prevent formation of monomethyl-monoprotonated species as by-products, addition of a hindered base (2,6-di-*tert*-butyl-4-methylpyridine) was necessary. The mixture of **2**·(TfO⁻)₂ and the pyridinium salt was treated with NaBH₄ to give bis(acridan) **6**. Oxidation of **6** with (*p*-BrC₆H₄)₃NSbCl₆ regenerated dication **2** as the SbCl₆⁻ salt. On the other hand, diacridine **1** was selectively monomethylated by MeOTf in benzene, and the resulting monocation was treated with NaBH₄ to give the unsymmetric acridan-acridine hybrid **3**, which was further methylated to give the acridan-acridinium complex **4**·TfO⁻. Selective monomethylation in benzene could be accounted for by insolubility of the resulting monocation salt in this solvent. We unexpectedly found that, under aerated alkaline conditions,



Scheme 1 Preparation of acenaphthylene-1,2-diylideneacridine **1** and its derivatives **2-6**.



4-TfO⁻ can be transformed into peroxide **5**. Although the precise reaction mechanism of formation of peroxide is still unclear, it might include deprotonation of the methine proton of acridan to form neutral acenaphthenequinodimethane **9** followed by reaction with oxygen. Peroxide formation from an electron-donating tetraarylacenaphthenequinodimethane was previously reported by our group.¹⁸

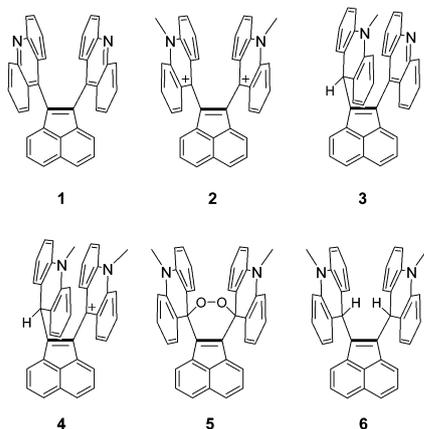


Fig. 2 shows an ORTEP drawing of **1** obtained by low-temperature single-crystal X-ray analyses. Selected structural parameters around the C₁=C₂ bond are summarized in Table 1. The precisely determined C₁=C₂ bond length in **1** [1.3789(19) Å] is clearly much greater than the standard value (1.33 Å) and that in the parent acenaphthylene. Notably, the C₁=C₂ bond in **1** is longer than that in 1,2-di-*tert*-butyl-3,3,5,5-tetramethylcyclopentene [1.365(2) Å], which is the

sole successful example of a long C=C bond without disturbing the sp²-hybridized nature or π-bond order.¹⁹ As shown by the space-filling model of **1** (Fig. 2), the acridine π units are in strong contact with each other in a parallel fashion. Especially, the C9'...C9'' distance (3.19 Å) is much shorter than the sum of the van der Waals radii (3.40 Å). The torsion angles between acenaphthylene and the two acridines (62.7° and 64.0°, respectively) are large enough to neglect π-conjugation between the acridine units and the C₁=C₂ bond. The C₁=C₂ bond in **1** is significantly longer than the C₁=C₂ bond length in 1,2-di(1-naphthyl)acenaphthylene [1.367(2) Å],²⁰ in which the naphthalene units are arranged in an anti-parallel fashion to reduce steric repulsion. Thus, very severe steric repulsion should be the main contributor to elongation of the C₁=C₂ bond. As designed, different modes of deformation, such as twisting or pyramidalization, seldom occur in **1**, and thus the C₁=C₂ unit is almost planar, as shown by the small torsion angles of C₉-C₁-C₂-C_{9'} (X) and C_{8a}-C₁-C₂-C_{2a} (Y) and by the fact that the sums of the bond angles around C₁ and C₂ (α + β + γ) are 360° (see Table 1).

The C₁=C₂ bond length [1.377(3) Å] and other structural parameters of **1** in the CHCl₃ solvate crystal are similar to those of the nonsolvated crystal of **1** shown above (Table 1) despite the difference in the nature of their packing. Thus, the molecular geometry with the elongated C₁=C₂ bond is intrinsic to **1** rather than forced by crystal packing or other intermolecular factors.

To further confirm that π-conjugation is not responsible for elongation of the C₁=C₂ bond in **1**, the length of the C₁=C₂ bond was compared to those in its derivatives **2–6**. The electron-withdrawing nature of acridiniums in **2** is much higher than that of neutral acridines in **1**. If the electronic contribution from the substituents attached to the C=C bond is the major factor, the C₁=C₂ bond length of dication **2** should be different from that of **1**. However, the C₁=C₂ bond lengths of the two pseudopolymorphs of **2** [1.391(12) Å for the CHCl₃ solvate crystal; 1.371(5) Å for the MeCN solvate crystal] determined by low-temperature X-ray analyses were nearly the same as that of **1**, as were other structural parameters (Table 1), which can be rationalized by considering that acridinium and acridine have a similar steric bulkiness around the C₉-position. Thus, the contribution of an electronic effect to elongation of the C₁=C₂ bond should be negligible.

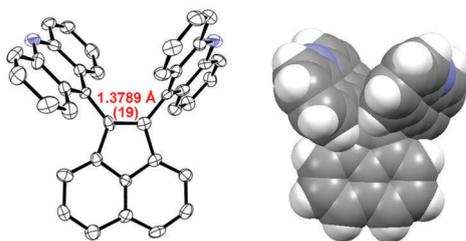
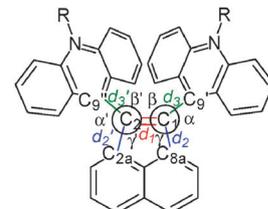


Fig. 2 ORTEP drawing (left) and the space-filling model of **1**.

Table 1 Selected structural parameters around the C₁=C₂ bond determined by low-temperature X-ray analyses or DFT optimizations

Compd	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₂ '	<i>d</i> ₃ '	α + β + γ	α' + β' + γ'	X	Y	C ₉ '...C ₉ ''
1	1.3789(19)	1.474(3)	1.489(3)	1.474(3)	1.489(3)	359.94(16)	359.94(16)	6.3(4)	1.0(3)	3.189(3)
1-CHCl₃	1.377(3)	1.479(3)	1.478(3)	1.481(3)	1.487(3)	359.98(17)	360.00(18)	1.8(4)	0.63(19)	3.249(3)
1 (calc)	1.383	1.482	1.485	1.482	1.485	360.0	360.0	0.34	1.01	3.232
2-MeCN	1.371(5)	1.475(4)	1.480(5)	1.480(4)	1.479(4)	359.9(3)	359.9(3)	4.4(4)	1.8(3)	3.115(5)
2-CHCl₃	1.391(12)	1.499(10)	1.464(10)	1.482(9)	1.484(12)	359.9(8)	359.9(8)	6.8(10)	0.4(6)	3.172(13)
2 (calc)	1.397	1.474	1.481	1.474	1.482	360.0	360.0	0.70	1.53	3.268
3	1.369(4)	1.474(5)	1.480(4)	1.479(4)	1.525(5)	360.0(3)	360.0(3)	3.9(5)	0.3(3)	3.259(4)
3 (calc)	1.377	1.482	1.487	1.484	1.527	360.0	360.0	0.62	0.06	3.342
4 (mol 1)	1.374(10)	1.488(10)	1.464(10)	1.477(10)	1.528(10)	359.9 (6)	360.0(6)	1.5(13)	1.6(8)	3.288(10)
4 (mol 2)	1.357(10)	1.503(10)	1.489(9)	1.466(10)	1.504(10)	360.0(6)	360.0(6)	1.6(13)	1.7(8)	3.262(9)
4 (calc)	1.380	1.482	1.478	1.479	1.526	360.0	360.0	0.61	1.04	3.300
5	1.356(5)	1.478(6)	1.501(6)	1.477(6)	1.505(6)	360.0(4)	359.8(4)	8.4(5)	2.7(4)	3.015(4)
5 (calc)	1.369	1.477	1.509	1.477	1.509	360.0	360.0	5.04	2.46	2.988
6	1.364(4)	1.479(3)	1.500(3)	1.486(3)	1.511(4)	360.0(2)	360.0(2)	6.7(5)	2.3(4)	3.175(4)
6 (calc)	1.377	1.483	1.510	1.484	1.521	360.0	360.0	0.00	0.00	3.207

X: torsion angle of C₉'-C₁-C₂-C₉''; Y: torsion angle of C_{8a}-C₁-C₂-C_{2a}.



In addition, further evidence of the absence of conjugation effects could be obtained by comparison of the $C_1=C_2$ bond lengths of **1** and **2** with those of push-pull type compounds **3** and **4**, in which one of the two acridine/acridinium units is replaced by an electron-donating acridan unit. In general, push-pull substitution over the $C=C$ bond causes a drastic decrease in the π -bond order, and thus the bond length must be much longer in the presence of conjugation effects between the substituents over $C_1=C_2$, especially in **4**, in which the acridinium is more strongly electron-accepting than the acridine in **3**. However, the observed $C_1=C_2$ bond lengths of **3** [1.369(4) Å] and **4** [1.374(10) Å and 1.357(10) Å; two independent molecules] are similar or rather shorter than those in diacridine **1** and diacridinium **2**, which clearly excludes the presence of conjugation effects in the present system. The notable difference in d_3' can be explained by the fact that the standard Csp^2-Csp^3 single bond is longer than the Csp^2-Csp^2 single bond.

In the case of peroxide **5** and diacridan **6**, steric repulsion between two methylacridan units was obviously relieved by the insertion of two oxygen or hydrogen atoms between the bulky methylacridan units. The $C_1=C_2$ bond lengths [1.356(5) for **5** and 1.364(4) Å for **6**, respectively] became shorter than that in diacridine **1**, and are almost the same as that in nonsubstituted acenaphthylene. Based on all of these experimental results, we can safely conclude that steric repulsion is the dominant factor in the elongation of the $C=C$ bond in **1**. The structures of **1-6** optimized by DFT calculations (B3LYP/6-31G*) well reproduced those determined experimentally by X-ray analyses, which supports the steric effect for the elongation of the $C_1=C_2$ bond in **1**.

In summary, we have demonstrated that steric repulsion in **1** effectively elongated the pure $C=C$ double bond by a rational molecular design, in which we could rule out the influence of a π -conjugating electronic effect. The key to success was the use of bulky planar groups to cause severe steric repulsion which could only be relieved by bond elongation, and not by other modes of deformation. Diacridine **1** has a long $C=C$ bond of up to 1.3798(19) Å, which is much longer than the standard value. The exclusion of both the conjugation effect and structural deformation guarantees the sp^2 -hybridized nature and the lack of electronic perturbation for these pure $C=C$ double bonds. As molecules with unusual $C=C$ bonds are developed, their characteristic physical and electronic properties (e.g., small force constant and long wave absorption involving a long $C=C$ bond) and unique reactivities will be investigated. Studies along these lines will be made in due course.

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