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1,2-Diarylindano[*a*]indane: A Molecule with Skewed, Cofacially Disposed Aromatic Moieties and a Long C–C Single Bond

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Abstract: 1-(4-Methoxyphenyl)-2-(4-nitrophenyl)-5,10-dimethoxyindano[1,2-*a*]indane (**6**) is a new system with a long carbon–carbon single bond arising from through-bond coupling. The versatility and simplicity of the aromatic molecular framework of this system suggests that it may be useful for the study of substituent effects on through-bond coupling, stacking between aromatic rings, charge-transfer, and carbon–carbon bond cleavage. Indanoindane **6** was prepared by bis-C-alkylation of 1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethanone with 3-methoxybenzyl chloride, followed by double cyclization–dehydration. X-ray crystallography revealed that the indanoindane chassis of **6** was bent at the central single carbon–carbon single bond, with the two five-membered rings adopting a distorted envelope conformation. The priapic 4-methoxyphenyl and 4-nitrophenyl substituents attached to the central ethane unit are staggered with respect to each other, producing a skewed, cofacial array, with a centroid to centroid distance of 4.13 Å; these two rings are 2.93 Å apart at their closest point. The most remarkable structural feature of **6** is the elongated (1.618 Å) central carbon–carbon single bond. Molecular mechanics energy minimizations were unable to reproduce this value, whereas the AM1 molecular orbital method predicted a length of 1.614 Å. The Mulliken overlap population of the central single bond increased if methyl groups replaced either or both priapic aromatic substituents in the calculations. These results suggest that through-bond coupling is the origin of the central bond elongation. AM1 calculations indicated that the length of the central bond in **6** and in a model system is not significantly altered by the nature of the para substituents on the priapic aromatic rings. A survey of the crystallographic data on other indanoindanes demonstrated that central single-bond elongation is not a general characteristic of the indanoindane skeleton. Relative to a composite absorption spectrum of its constituent chromophores (*p*-alkylanisole, *p*-alkylnitrobenzene, and 5-methoxyindane), the absorption band of **6** is slightly more intense, slightly red-shifted, and wider and has a prominent red-edge tail. These changes in the UV spectrum of **6** are ascribed to a weak charge-transfer interaction between the priapic rings.

Introduction

Molecules that impose a face to face juxtaposition of aromatic rings have been the subject of much investigation. Such systems provide models for the study of charge-transfer processes,[1] $\pi-\pi$ transannular interactions,[2] bonding and strain,[3] and stacking.[4] Most of these studies have involved variation of the donor/acceptor pair and in the distance and orientation of the aromatic moieties. Herein, we report the use of indano[*a*]indane as a chassis for the attachment of aryl substituents. This system provides a close, but skewed, juxtaposition of the aryl rings.

Table I. Selected Bond Angles in Indanoindane **6**[a]

angle	deg	angle	deg
C1–C2–C3	119.1	C5–C13–C23	114.4
C2–C3–C4	129.0	C13–C23–C24	122.5
C2–C1–C16	120.5	C23–C24–C25	131.7
C4–C5–C17	111.8	C24–C25–C26	119.5
C5–C17–C18	122.3	C26–O5–C31	117.5
C17–C18–C19	122.3	C14–C13–C23	144.6
C18–C19–C20	118.3	C15–C14–C13	129.0
C20–N–O4	118.5	C15–C16–C1	120.3
O3–N–O4	123.5	O1–C1–C16	124.2
C4–C5–C13	102.0	C29–O1–C1	118.5
C5–C13–C14	102.3	C12–C13–C14	110.7

[a] The estimated average standard deviations for the bond angles are 0.2–0.5°.

In the course of our synthesis of fluorescent estrogen receptor ligands,[5] we isolated indano[*a*]indane **6** as a byproduct in the sequence in which the diarylindene **5** was the desired product (Scheme I). The structural assignment of indanoindane **6** was supported by mass, proton NMR, and infrared spectroscopy and elemental analysis and was confirmed by single-crystal X-ray crystallography. The yellow color of indanoindane **6** in solution suggested a charge-transfer interaction between the priapic[6] electron-rich methoxyphenyl and electron-deficient nitrophenyl groups. Herein, the synthesis of indanoindane **6**, its molecular structure, and its charge-transfer properties are described, and the structure obtained by X-ray crystallography is analyzed by molecular mechanics and semiempirical molecular orbital methods. The X-ray crystallographic structure determination of **6** indicated that this compound is a new system that displays a long carbon–carbon single bond. The origin of this bond elongation is discussed.

Results and Discussion

Synthesis. Our first attempt to intentionally prepare the precursor of indanoindane **6**, bisbenzyl ketone **3**, involve the alkylation

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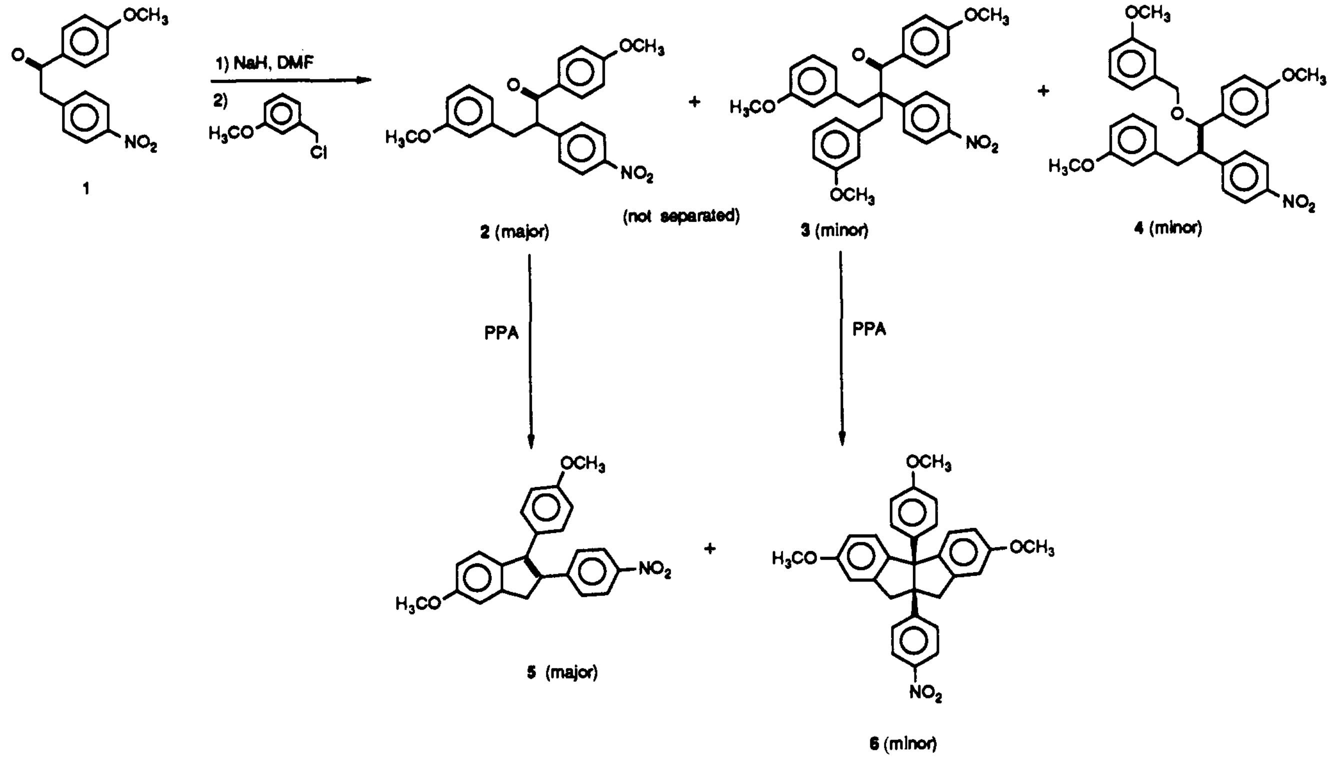
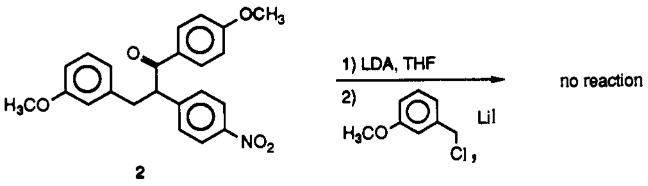
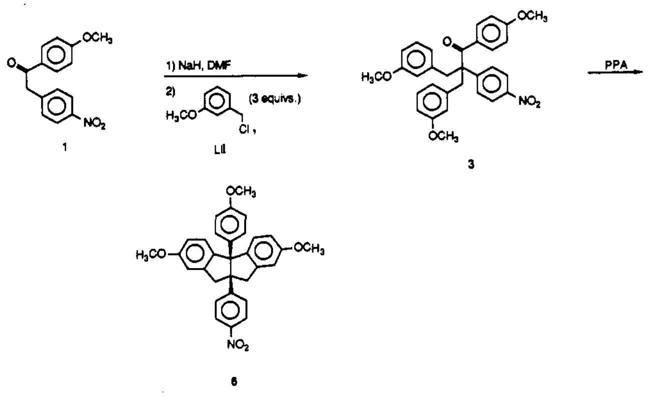
Scheme I



Scheme II



Scheme III



of the enolate of monobenzyl ketone **2**[5b] under conditions favoring C-alkylation (lithium counterion, THF) over O-alkylation.[7] However, no alkylation occurred (Scheme II).

By contrast, under conditions generally regarded as appropriate for O-alkylation (sodium enolate, DMF),[7] one-pot bis-C-benzylation of nitrodeoxybenzoin (**1**)[5b] was achieved in good yield (61%). Cyclization of this bisbenzyl ketone gave the expected indanoindane (Scheme III), via two successive Friedel–Crafts alkylations.[8]

Molecular Structure. The structure of indanoindane **6** obtained by X-ray crystallography appears in Figure 1. The atomic numbering scheme for indanoindane **6** and its skeletal bond lengths appear in Figure 2; bond angles are found in Table I.

The indano[*a*]indane system of **6** is bent at the central single bond (C5–C12) and is reminiscent of a butterfly.[9] The C–C bond lengths in the aromatic rings in the indano[*a*]indane system are not equivalent and do not show a clear pattern of alternation. The bridgehead bonds of the aromatic rings are not the longest bonds, in contrast to a Mills–Nixon effect.[10] The variation in the bond lengths is probably due to the usual deformations produced in arenes by the electronic properties of substituents.[11]

An interesting structural feature of **6** is the long (1.618 Å) central single bond (C13–C5), similar in length to the bonds of various photoisomers of linked polynuclear aromatics.[12] Normally, bonds between sp^3-hybridized carbons are 1.537 Å.[13] The origin of this elongation will be discussed in detail (vide infra).

The two five-membered rings adopt a distorted envelope conformation (see Figure 3). The C13–C14 and C12–C13 bonds of the cyclopentenes are slightly lengthened (1.522 and 1.529 Å, respectively), as compared to the distance expected for C_{sp^2}–C_{sp^3} bonds (1.505 Å).[13]

The two priapic rings are staggered with respect to each other; the C17–C5–C13–C23 torsional angle is 32.1°. The bonds between the priapic rings and the indano[*a*]indane system (C13–C23 and C5–C17) are elongated (1.523 and 1.522 Å), as compared to the normal 1.505-Å value. But despite the staggered conformation and bond elongation of C13–C23, C5–C17, and C5–C13, the closest distance between the priapic rings (C17 to C23; 2.93 Å) is less than the accepted van der Waals thickness (3.4 Å) of an aromatic ring.[15]

The structural features of aromatic nitro groups are dependent on the electronic properties of the other substituents in the aromatic

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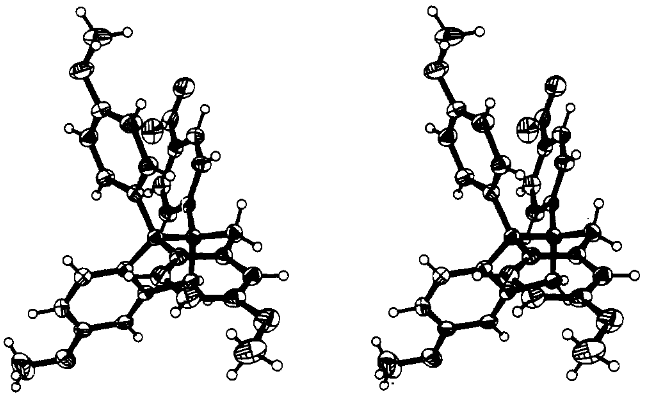

Figure 1. Relaxed stereoscopic thermal ellipsoid (35% probability) representation of indanoindane **6** plotted parallel to the best plane normal.

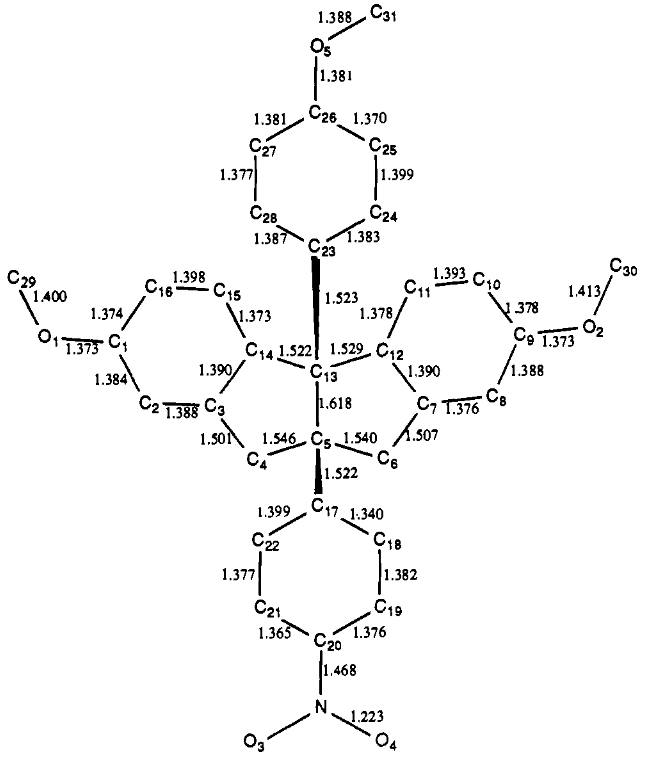

Figure 2. Atomic numbering scheme and bond lengths for indanoindane **6**. The estimated average standard deviations for the bond lengths are 0.003-0.006 Å.

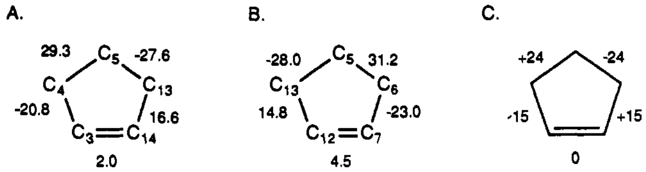

Figure 3. Comparison of the torsional angles (deg) of the C3-C4-C15-C13-C14 ring (A) and the C5-C6-C7-C12-C13 ring (B) with cyclopentene in an ideal envelope geometry[14] (C).

Table II. Structural Features of the Methoxy Groups in Indanoindane **6**

	priapic OCH_3	ind[*a*]ind OCH_3[a]	typical $ArOCH_3$[b]
O-CH_3 dist, Å	1.388	1.407	1.425
Ar-O dist, Å	1.381	1.373	1.371
Ar-O-CH_3 angle, deg	117.8	118.4	117.7

[a] Average value for the two methoxy groups attached to the indano[*a*]indane nucleus. [b] Average values for unexceptional methoxyarenes, as determined by X-ray crystallography.[17]

Table III. Central Bond Lengths after Energy Minimization Calculated for Indanoindane **6**

	length of C-C bond after minim,[a] Å	deviation from X-ray,[b] Å
TFF[c]	1.565	-0.053
MM2[d]	1.568	-0.050
AM1[e]	1.614	-0.004

[a] Length of C13-C5 bond after energy minimization. [b] Deviation of calculated C13-C5 bond length from the bond length (1.618 Å) obtained by X-ray crystallography. [c] Molecular mechanics using the Tripos force field. [d] Molecular mechanics using the MM2 force field. [e] AM1 semiempirical molecular orbital calculations.

Table IV. Comparison of Torsional Angles (deg) in the X-ray Crystallographic Structure of Indanoindane **6** and the AM1 Geometry Optimized Structure

torsional angle	X-ray	AM1
C5-C13-C23-C28	82.4	97.2
C13-C5-C17-C22	-91.8	-77.3
C5-C13-C14-C15	-165.5	-166.3
C2-C3-C4-C5	161.4	165.0
C17-C5-C13-C23	-32.1	-25.1

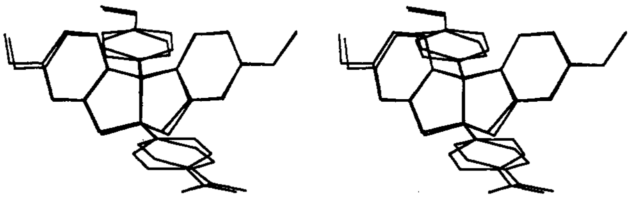

Figure 4. Relaxed stereoview of the superposition of the X-ray crystallographic structure of indanoindane **6** with AM1 energy minimized structure.

ring. The C-N bond length, at 1.468 Å, is shortened compared to that of 4-nitrotoluene, an effect similar to that produced by an electron-donating substituent at the para position.[16] The O-N-O angle is similar to that of 4-nitroaniline, but the N-O bond is shorter (1.223 vs 1.246 Å).[16] The structural parameters of the two different methoxy groups of **6** are compared to those observed in other methoxyarenes in Table II.

The quality of the crystal structure determination is satisfactory. The reliability index (*R* factor) is 0.043, and the estimated standard deviations for the elongated C13-C14, C12-C13, C13-C5, C13-C23, and C5-C17 bonds are all 0.003 Å.[18] Indanoindane **6** has no intermolecular contacts less than the sum of the van der Waals radii, so the observed solid-state structure is at or near a local energy minima.[19] The observed conformation of **6** may represent a global minimum because there is only one unique molecule per asymmetric unit[20] and the intermolecular forces are minimal.[21] In any case, bond angles, and especially bond lengths, are not appreciably affected by crystal lattice forces.[22] These considerations indicate that the bond elongations observed in **6** are not artifactual.

Origin of the C13-C5 Bond Lengthening. Unusually long C-C bond lengths[23] in hindered ethanes have been ascribed to steric

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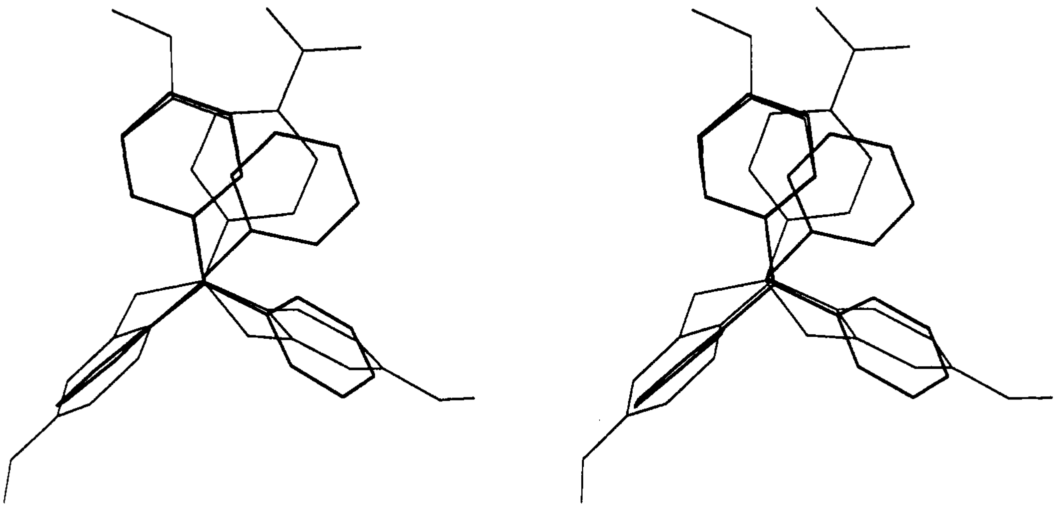


Figure 5. Relaxed stereoview of the superposition of the X-ray crystallographic structures of indanoindane **6** and 1,1,1,2-tetraphenylethane (TPE). The atoms involved in the fit were the central ethane carbons of both systems and the adjacent aromatic ring carbons (C1 of the 4-methoxyphenyl group of **6** and the first carbon of a phenyl group attached to C1 in TPE). TPE is bold relative to the indanoindane.

effects[24] or, in the case of adjacent π-systems,[25] to through-bond coupling (TBC).[26] The TBC phenomenon arises when multiple π-orbitals are essentially parallel to a central σ-bond.[27] In such a case, molecular mechanics methods, which do not consider this special electronic interaction, are unable to reproduce the long bond lengths. Molecular orbital approaches are more successful.[27] To determine the origin of the C13–C5 bond lengthening in indanoindane **6**, the energy of the X-ray crystallographic structure was calculated and the geometry was energy minimized by either of two molecular mechanics force fields (Tripos[28] and MM2[29]) or by the AM1 semiempirical molecular orbital method.[30] The results appear in Table III.

From Table III, the long bond length is well reproduced by the AM1 minimization,[31] whereas both force fields do poorly. However, the AM1 calculation is less successful in computing torsional angles (Table IV). The root mean square fit of all atoms in the crystal and AM1-minimized structures is 0.2340 Å (Figure 4).

To support the reliability of the AM1 minimization procedure, the central single bond of indanoindane **6** was fixed at a distance from 1.57 to 1.64 Å, in 0.01-Å increments. The constrained structures were then minimized (MM2), and the energies of the resulting structures were evaluated by the AM1 method. An energy well was found at 1.61 Å, in good agreement with the complete minimization value (1.614 Å) and the experimental value (1.618 Å). In contrast, an MNDO molecular orbital calculation[32] on **6** under the same constraints produced an energy minimum at 1.64 Å. Thus, in this case, the AM1 method outperforms the MNDO method in evaluating the bond length in a system that displays TBC. This is of interest because the MNDO method has been widely used to assess the presence of TBC.[3d]

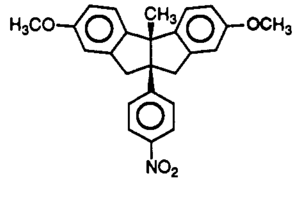
Table V. Overlap Populations of Indanoindane **6** and Its Analogues **7** and **8**[a]

	Mulliken overlap population		Mulliken overlap population
6	0.6548	**8a**	0.6660
7	0.6622	**8b**	0.6704

[a] The positions of the methyl groups were optimized while the rest of the molecule was fixed at the equilibrium AM1 geometry obtained for **6**.[33b]

Since the molecular orbital method has successfully reproduced the long bond whereas force field methods have failed, indanoindane **6** meets the operational definition of a molecule in which TBC exits.[25b,27,33] A more rigorous test of TBC is the evaluation of Mulliken overlap populations in analogues in which one of the π-components is replaced by a methyl group.[25b,27,33] Through-bond coupling is suggested if the Mulliken overlap population of the appropriate bond increases.

In the case of indanoindane **6**, AM1 calculations were carried out on its analogues **7**, **8a**, and **8b** in which a methyl group replaces the 4-methoxyphenyl, 4-nitrophenyl, or both substituents, respectively. As expected, the Mulliken overlap population increases (Table V), further supporting the existence of TBC in indanoindane **6**.



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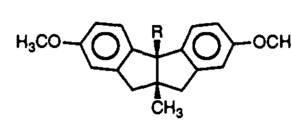

8a, R = 4-CH$_3$O-C$_6$H$_4$
b, R = CH$_3$

If the MM2 C5–C13 bond length of **6** is taken as a reference point (i.e., the bond length due to steric repulsions between the priapic rings), a TBC elongation of 0.050 Å is evident. However, the MM2 force field calculates C–C bond lengths as too short in the case of elipsed or near-eclipsed bonds.[34] Nevertheless, this

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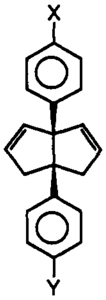


9, X = Y = H
10, X = Y, = NO_2
11, X = Y, = NH_2
12, X = Y = OCH_3
13, X = OCH_3, Y = NO_2

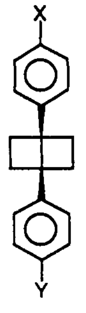
Figure 6. Model systems for indanoindane **6** to determine the effect of para substitution on the central σ-bond length. AM1 MO calculations provide a central σ-bond length of 1.604 Å for **9**; for **10–13**, this length was 1.605 Å.

deviation is typically only 0.01–0.015 Å.[34] Thus, the TBC effect proposed for **6** is not simply an artifact of inadequate force field parameterization.

The molecular structures of sterically hindered polyphenylethanes have been the subject of much study.[23c,35] Stripped of its auxochromic groups, indanoindane **6** is a locked (cross-clamped)[23c] 1,1,1,2-tetraphenylethane. The X-ray crystallographic structure of indanoindane **6** is overlaid with that of 1,1,1,2-tetraphenylethane (TPE)[35f] in Figure 5. The methylene bridges in **6** produce a profound effect on the overall molecular geometry, with a loss of the characteristic propeller conformation of the triarylmethane fragment[36] and a compression in the torsional angle between two of the vicinal aryl groups. Also, in TPE, a much smaller bond-lengthening effect is evident (TPE ethane C–C bond length = 1.567 Å).[35f] Thus, as observed elsewhere,[23c] rigidifying the molecular framework, as in **6**, accentuates the TBC effect.

The para-oriented electron-donating methoxy group and electron-withdrawing nitro group produce a push–pull combination that may strengthen the TBC interaction and thereby lengthen the bond.[3d] However, AM1 MO calculations on the model system for indanoindane **6** in which the character of the para substituent is varied over a limited range (systems **9–13**) do not suggest a significant remote electronic effect on the central σ-bond length (Figure 6).

These results are contrary to those of Osawa and co-workers, who performed MNDO calculations of 1,4-disubstituted bicyclo[2.2.0]hexanes (**14**).[33b] In their system, a definite substituent effect on bond length, HOMO level, and electron population was observed. However, the prestrain of bicyclo[2.2.0]hexane may enhance the effect in their case.[3d]



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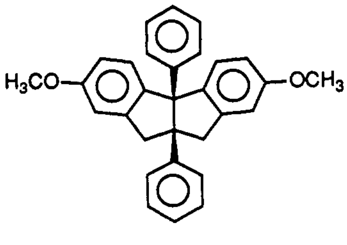
The smaller size of model system **9** made it amenable to ab initio molecular orbital calculations in the STO-3G level.[37] The central single bond was fixed at a distance of 1.57–1.64 Å in 0.01-Å increments, the structure was minimized by MM2, and the energy was evaluated by STO-3G. An energy minimum was observed at 1.60 vs 1.61 Å for the analogous AM1 computation. Thus, with this system, the AM1 method provides satisfactory agreement with STO-3G.

We have also performed total geometry optimization by the AM1 method on a close analogue (**15**) of indanoindane **6**, in which hydrogens replace the substituents on the priapic rings. The length of the central carbon–carbon single bond in **15** was found to be 1.610 vs 1.614 Å for the comparable (AM1) bond length in **6**. Thus, in the indanoindane system, it appears that the remote push–pull substituents (4-methoxy and 4-nitro) cause little elongation of the central single bond. In this regard, experimental structure analysis of **15** would be particularly informative and, with 6, would provide the first direct experimental comparison of TBC in systems with and without push–pull substitution.



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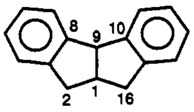
Factors Affecting Bond Elongation in 6. Although the C13–C5 bond distance in indanoindane **6** is considerably longer than typical C_{sp^3}–C_{sp^3} bonds, it is not as dramatic as in certain compounds that display TBC.[3d] Thus, an examination of the structural factors that influence TBC in **6** is in order.

If the central σ-bond is strained by other geometric features in the molecule, TBC is enhanced.[3d] To evaluate the inherent strain present in the parent indanoindane system (**16**), which may contribute to TBC, the precent p character of the hybrid orbitals that form the central σ-bond in **16** was assessed.[38]



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The p character was determined from the published bond angles θ of **16**[39] and the relation $\cos\theta = (P - 1)/P$, where P is the fractional p character of the hybrid orbitals forming the bond.[40] Thus, C9 bonds to C1 with a hybrid typical of 81% p character; C1 bonds to C9 with a hybrid orbital of 78% p character. This is only a modest enhancement over the ideal 75% p character expected in sp^3 hybridization. Thus, prestrain is not significant in the parent indanoindane skeleton and is not a large contributor to bond elongation in indanoindane **6**.

Other factors may attenuate bond elongation in **6** as well. For maximum TBC, a trans configuration of the π-components is necessary.[41] The 5-5 ring fusion of indanoindane **6** requires a cis configuration. For molecules with three intervening σ-bonds between the π-components, as in **6**, through-space coupling opposes through-bond coupling.[31a] The close distance between the priapic rings in indanoindane **6** (2.93 Å between C23 and C17) may allow some through-space coupling to occur, which is negligible beyond 3.0 Å.[41]

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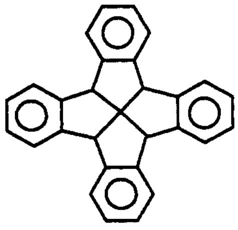
Indanoindane **6** is only partially rigid. Annelation of the priapic rings may result in further TBC.[3d,35a] Also, the central σ-bond of **6** is aligned with only two π-centers. (As the number of π-systems parallel to the σ-bond increases, bond elongation increases.)[27] Furthermore, the skewed cofacial arrangement of the priapic rings in **6** decreases π-orbital alignment with the central σ-bond, decreasing TBC. Despite all of these factors that tend to decrease TBC in indanoindane **6**, it is a new member of the small group of compounds in which TBC has been demonstrated.[3d] Thus, the results obtained for **6** suggest that moderate through-bond coupling can occur between vicinal aryl groups attached to an unstrained bond if the molecule is partially rigidified. The AM1 data indicate that the push-pull substitution of **6** makes only a small contribution to the central bond elongation.

Consequences of Bond Elongation. The effect of the bond elongation in indanoindane **6** on the bond energy and bond order can be estimated by simple empirical relationships. The central σ-bond is elongated by 0.082 Å as compared to the C–C bond length in ethane.[42] For each 0.0025-Å increase in bond length, the bond energy decreased by 1 kcal/mol.[42] Thus, for **6**, a reduction of ~33 kcal/mol is expected. Ethane has a C–C bond energy of 88 kcal/mol.[42] Thus, a bond energy on the order of 55 kcal/mol is expected for **6**. This is comparable to the C–I bond energy.[43]

The 0.082-Å bond elongation would provide a bond order of 0.77, from the equation $\Delta d = -0.71 \log n$, where, Δd is the change in bond length and n is the bond order.[44] These considerations and the general observation that C–C bond lengths greater than 1.6 Å are prone to cleavage[3d] suggest that indanoindane **6** may have interesting avenues of reactivity available to it. However, the stability of **6** is undoubtedly enhanced by the cross-clamping of the ethane carbons.[23c]

Comparison of Other Indanoindanes. To determine if the lengthening of the central single bond in indanoindane **6** was a common feature of an indano[1,2-*a*]indane ring system, the Cambridge Structural Data Base[45] and CAS Online were searched for molecules containing this structural fragment; five molecules with crystal structure data were available (**16**–**20**). In fenestrindan (**17**),[46] ferretane (**18**),[47] the tetrabenzopentacycle **19**,[14] and indanoindane (**16**),[39] the lengths of the corresponding bonds are 1.551, 1.558, 1.559, and 1.553 Å, respectively, vs the typical C_{sp^3}–C_{sp^3} bond length of 1.537 Å.[13] Thus, only a small elongation effect is operative in these systems, as compared to indanoindane **6**.



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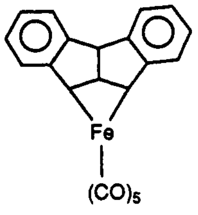

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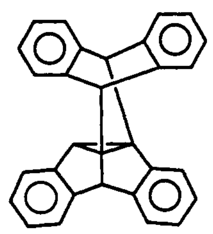

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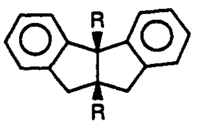

16, R = H
20, R = Br

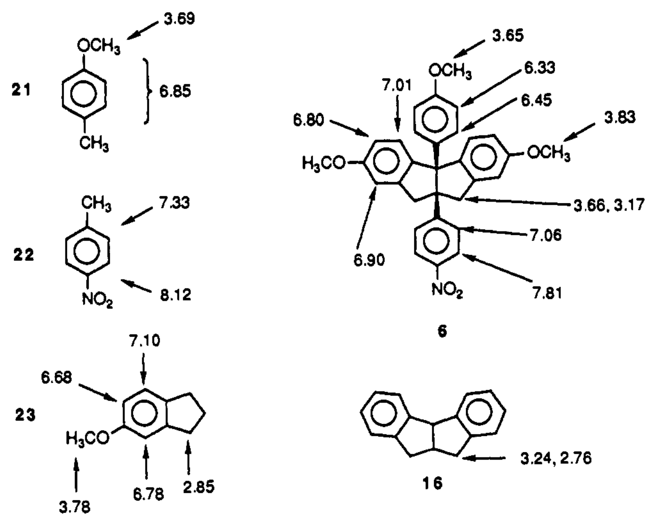

Figure 7. Field positions of protons on the indicated carbons in indanoindane **6** compared to model compounds.[49,51,52] Shifts are on the δ scale.

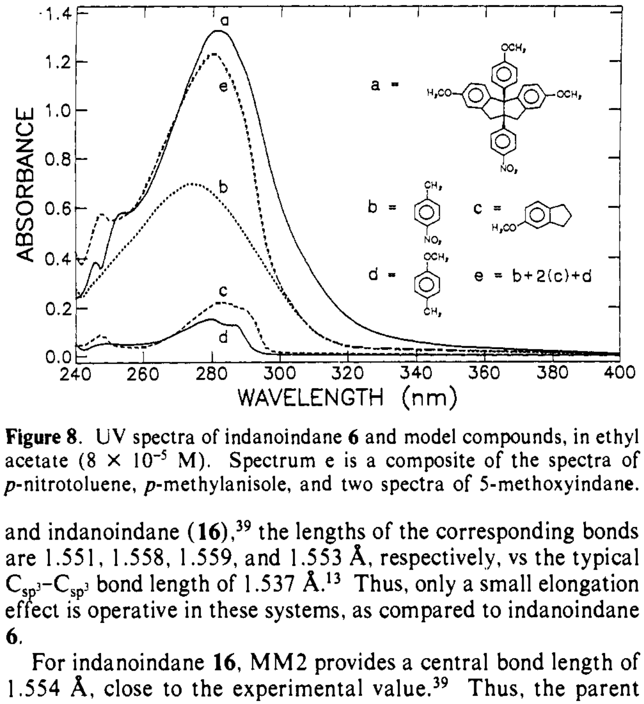

Figure 8. UV spectra of indanoindane **6** and model compounds, in ethyl acetate (8 × 10^{-5} M). Spectrum e is a composite of the spectra of *p*-nitrotoluene, *p*-methylanisole, and two spectra of 5-methoxyindane.

For indanoindane **16**, MM2 provides a central bond length of 1.554 Å, close to the experimental value.[39] Thus, the parent indanoindane system has no special electronic features that cannot be accounted for in the molecular mechanisms force field. In *cis*-dibromoindanoindane (**20**), the central bond is a long 1.583 Å.[9] Elongated bonds have previously been reported in polyhalogenated hydrocarbons.[3d,48] The MM2 force field produces a value of 1.562 Å, indicating the bond elongation in **20** may be due to specific electronic factors that are not modeled by the MM2 method. Alternatively, the relatively small difference between the experimental and MM2 values for **20** may be due to inadequate force field parameterization for the carbon–bromide bonds.[48c]

Proton NMR Spectrum. The proton NMR spectrum of indanoindane **6** shows large upfield shifts (ca. 0.3–0.5 ppm) for the protons on both priapic rings relative to model compounds[49] (Figure 7). The cofacial disposition of the priapic rings produces this condition of mutual shielding. Such upfield shifts have also

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Table VI. Absorbance Properties of Indanoindane **6** and Model Compounds[a]

	λ, nm	ν, cm^{-1}	ϵ
indanoindane **6**	282	35 500	17 600
p-methylanisole (**21**)	280, 286	35 700, 35 000	1940, 1610
p-nitrotoluene (**22**)	274	36 500	8710
5-methoxyindane (**23**)	284, 292 (sh)	35 200, 34 200	2770, 2080
composite (**21** + **22** + 2(**23**))	280	35 700	*b*

[a] In ethyl acetate. [b] Not applicable.

Table VII. Distance between Corresponding Points on Cofacially Disposed Rings for Compounds in Figure 9

	distance, Å		
compd	p–p[a]	d–d[b]	c–c[c]
dibromojanusene[d]	2.99	4.09	*e*
indano[*a*]indane **6**	2.93	5.35	4.13
1,8-diphenylnaphthalene[f]	2.99	*e*	*e*
[2.2]paracyclophane	2.89[g]	3.10[g]	3.09[h]

[a] Distance between proximal carbons. [b] Distance between distal carbons. [c] Distance between the centroids of the cofacial rings. [d] Reference 56. [e] Not available. [f] Reference 3c. [g] Reference 1e. [h] Reference 57.

been observed in other systems with cofacial aryl rings; in 1,8-diphenylnaphthalene, the protons of the phenyl substituents experience a 0.53 ppm upfield shift.[50] The methylene protons of **6** are shifted considerably downfield relative to indane (**23**)[51] or unsubstituted indanoindane (**16**).[52] This deshielding is probably not due to the priapic aromatic ring at C5, but is the usual effect for an electron-withdrawing group at this position of an indanoindane.[53]

UV Spectra and Charge Transfer. Indanoindane **6** contains three alkyl-substituted anisole chromophores and a 4-alkylnitrobenzene chromophore. However, the UV spectrum of **6** is not a simple composite of the four chromophores (see Figures 8 and Table VI). Relative to the sum of the spectra of model compounds *p*-methylanisole (**21**), *p*-nitrotoluene (**22**), and 5-methoxyindane (**23**), the spectrum of **6** displays a slight bathochromic shift (200 cm^{-1}), a small hyperchromic effect, red-edge tailing, and a significant increase in bandwidth. This may be due to a weak charge-transfer (CT) interaction[2,54] between the electron-rich priapic anisole unit and the electron-deficient nitrobenzene group.

The weak nature of the CT interaction may have several origins. First, nitrobenzene is a weak acceptor in intermolecular CT complexes.[55] The orientation of the donor/acceptor substituents also has a strong influence on the extent of charge transfer.[1b] Furthermore, the skewed disposition and the distance between the priapic chromophores decreases interaction by a through-space mechanism. A through-bond interaction is limited by the absence of an all-trans σ-bond geometry between the donor and acceptor in **6**.[26,41]

Comparison with Other Systems with Cofacial Aromatic Rings. Various classes of compounds have been prepared in which aromatic rings are constrained to an approximate cofacial disposition. Several representative compounds appear in Figure 9. The geometry of the cofacial rings in these systems can be compared by measuring the intramolecular distances at corresponding points on each of the cofacial rings (Table VII). However, the cyclophanes cannot be compared directly to the other compounds of this type because of the severe skeletal deformations that occur in the aromatic rings.[1d]

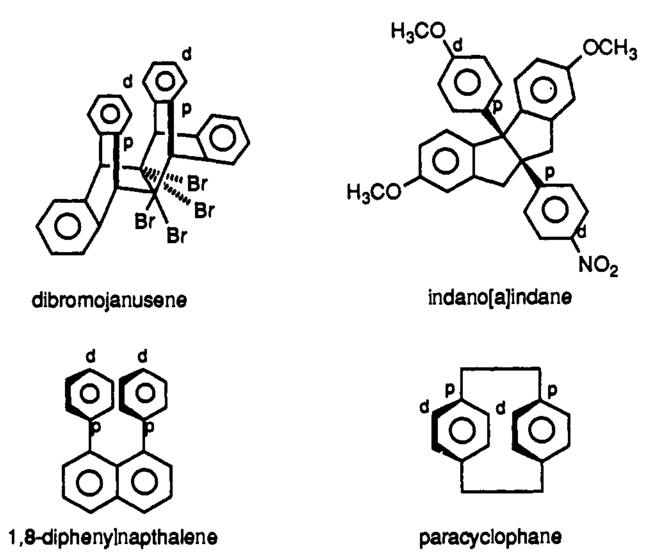

Figure 9. Examples of compounds with approximately cofacial aromatic rings. The letters p and d refer to proximal and distal.

The diarylindanonindane **6** differs from the noncyclophane systems in that the proximal ring carbons are closely spaced, but the distal ring carbons are much further apart. Thus, the indanoindane framework provides a novel spatial disposition for the appended aryl moieties, which may be of interest in studies of the geometric dependence of charge transfer[1] and transannular interactions.[2]

Conclusions

Indanoindane **6** is the first example of a locked 1,1,1,2-tetraphenylethane. X-ray crystallography of **6** indicates a long (1.618-Å) carbon–carbon central bond. Molecular mechanics and molecular orbital calculations suggest that this bond elongation arises from through-bond coupling of the pendant aryl rings.

The molecular structure of the 1,2-diarylindanoindane system, with its apposed priapic rings and flanking fused arenes, may provide a useful vehicle for the study of physical organic phenomena. By varying the substituents on the priapic or flanking aromatic rings, the structural subtleties and reactivity patterns of molecules with through-bond coupling may be investigated. Also, functionalization of both flanking and priapic sites presents the opportunity to elaborate the 1,2-diarylindanoindanes into novel molecular recognition systems.[58,59] With its donor and acceptor fragments connected by an ethane link, indanoindane **6** may be an appropriate system for the investigation of the mesolytic cleavage of carbon–carbon bonds.[60] Such studies will be facilitated by the ready synthetic accessibility of substituted deoxybenzoins,[61] which compose the central bond/priapic ring keystone of the 1,2-diarylindanoindane system.

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Table VIII. Crystal Data for Indanoindane **6**

formula	$C_{31}H_{27}NO_5$
cryst syst	triclinic
space gp	$P\bar{1}$
a, Å	10.845 (4)
b, Å	12.421 (4)
c, Å	10.539 (3)
α, deg	94.65 (3)
β, deg	106.42 (3)
γ, deg	109.28 (3)
V, Å^3	1261.3 (7)
Z	2
density calcd, g/cm^2	1.299
crystallizing solvent	methanol
crystal habit	prismatic (yellow)
cryst dimens, mm	0.34 × 0.42 × 0.58
μ, cm^{-1}	0.82
transmission factor range	0.972–0.953
extinction	not applied
2θ limit, deg (octants)	46 ($\pm h \pm k \pm l$)
intensities (unique, R_i)	3384 (3510, 0.012)
intensities > $2.58\sigma(I)$	1910
R	0.043
R_w [for $w = 1/\sigma^2(F_o) + pF_o^2$]	0.057 (p = 0.02)
max density in ΔF map, e/Å^3	0.17

Experimental Section

General Data. Melting points (uncorrected) were determined on a Thomas-Hoover apparatus. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel F-254 glass-backed plates. Flash chromatography[62] was done with use of Woelm 32-63-μm silica gel.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a General Electric QE-300 (300-MHz) spectrometer; chemical shifts are reported downfield from a tetramethylsilane internal standard (δ-scale). Infrared (IR) spectra were obtained in chloroform on a Nicolet 700 spectrometer: prominent and diagnostic peaks are reported. Ultraviolet (UV) spectra were determined with a Hewlett-Packard 8451A spectrophotometer. Low-resolution mass spectra (MS) were done in the electron-impact mode on the Varian CH-5 spectrometer. The reported data are from an electron energy of 70 eV and follow the form of m/z (intensity relative to base peak = 100). Elemental analyses were performed by the Microanalytical Service Laboratory of the University of Illinois. The SYBYL molecular modeling system (Version 5.2),[28] was used for molecular graphics superpositions, molecular mechanics (Tripos Force Field) calculations, and Cambridge Structural Data Base searches. AM1 and MNDO calculations were performed with the MOPAC program (Version 5.0).[63] Ab initio calculations were performed with the GAUSSIAN80-USCF program.[64] Input files for the molecular orbital calculations were generated by the SYBYL system. MACROMODEL (Version 2.5)[65] was used for the MM2 calculations. The SYBYL and MACROMODEL software were operated on a MicroVax 2000 computer.

A standard procedure for product isolation was used: quenching by addition of water or an aqueous solution and exhaustive extraction with EtOAc, washing their extracts, drying with $MgSO_4$, and evaporating the solvent under reduced pressure. The quenching media, extraction solvent, and aqueous washes are noted after "product isolation".

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)-2-(3-methoxybenzyl)-3-(3-methoxyphenyl)-1-propanone (3). Sodium hydride (410 mg, 8.54 mmol, 50% dispersion in oil) was rinsed with hexane and suspended in DMF (5 mL). Nitrodeoxybenzoin (**1**)[5b] (1.0 g, 3.69 mmol), dissolved in DMF (15 mL), was added dropwise over 15 min. The enolate was generated over 3 h. Lithium iodide (60 mg, 0.45 mmol) and 3-methoxybenzyl chloride (2.3 g, 14.7 mmol) were added sequentially. The solution was heated at 60 °C for 48 h. Product isolation (5% HCl, EtOAc, brine) followed by flash chromatography (19:1 hexane–EtOAc, then 9:1 hexane–EtOAc) afforded a white solid (1.15 g, 61%) with a slightly higher R_f than the starting ketone: mp 76–78 °C; IR 1670, 1600, 1520, 1350, 1260, 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.10 (d, 2 H, J = 9 Hz, ArH ortho to $-NO_2$), 7.58 (d, 2 H, J = 9 Hz, ArH ortho to –CO), 7.23 (d, 2 H, J = 9 Hz, ArH meta to $-NO_2$), 7.03 (t, 2 H, J = 9 Hz, ArH meta to $-CH_2-$), 6.75 (d, 2 H, J = 9 Hz, ArH meta to –CO–), 6.68 (dd, 2 H, J = 9, 2 Hz, ArH para to $-CH_2-$), 6.41 (d, 2 H, J = 9 Hz, ArH para to $-OCH_3$), 6.36 (d, 2 H, J = 2 Hz, ArH ortho to $-CH_2-$, $-OCH_3$), 3.81 (s, 3 H, –COAr-OCH_3), 3.62 (s, 6 H, two –OCH_3), 3.51 (ABq, 4 H, J = 18 Hz, two $-CH_2-$); MS, 511 (1, M$^+$), 390 (1), 256 (4), 135 (100), 121 (13). Anal. Calcd for $C_{31}H_{29}NO_6$: C, 72.78; H, 5.71; N, 2.79. Found: C, 72.93; H, 5.77; N, 2.59.

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)-5,10-dimethoxyindano[1,2-*a*]indane (6). Bisbenzyl ketone **3** (366 mg) was mixed with polyphosphoric acid (PPA, 20 g), and the mixture was stirred mechanically under nitrogen at 40 °C for 19 h. Product isolation (ice–water, EtOAc, brine) and recrystallization from methanol at −30 °C provided a maize-colored, microcrystalline solid (153 mg, 43%). The sample for X-ray crystallography was obtained by slow evaporation of a methanol solution at 3 °C: mp 213.5–214.5 °C; IR 1605, 1510, 1350, 1250, 1045 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81 (d, 2 H, J = 9 Hz, ArH ortho to $-NO_2$), 7.06 (d, 2 H, J = 9 Hz, ArH meta to $-NO_2$), 7.01 (d, 2 H, J = 8 Hz, two ArH meta to $-CH_2-$), 6.90 (d, 2 H, J = 1 Hz, two ArH ortho to $-CH_2-$), 6.80 (dd, 2 H, J = 8, 2 Hz, two ArH para to $-CH_2-$), 6.45 (d, 2 H, J = 9 Hz, ArH meta to $-OCH_3$ on pendant ring), 6.33 (d, 2 H, J = 9 Hz, ArH ortho to $-OCH_3$ on pendant ring), 3.83 (s, 6 H, two –OCH_3), 3.66 (d, 2 H, J = 16 Hz, two –CH of $-CH_2-$), 3.65 (s, 3 H, –OCH_3), 3.17 (d, 2 H, J = 16 Hz, two –CH– of $-CH_2-$); MS 493 (100, M$^+$), 385 (21), 372 (41), 357 (16), 344 (29), 326 (7), 239 (9). Anal. Calcd for $C_{31}H_{27}NO_5$: C, 75.44; H, 5.51; N, 2.84. Found: C, 75.52; H, 5.56; N, 2.74.

X-ray Crystallography. Crystals of indanoindane **6** were grown by slow evaporation at 3 °C. Diffraction experiments were performed at room temperature with Mo radiation ($\lambda(K\bar{\alpha})$ = 0.71069 Å). Final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections (2θ > 21°). Three reference reflections monitored during each experiment showed no significant variation. Intensity data was corrected for Lorentz and polarization effects. Crystal data are listed in Table VIII. The average values and probability distribution of the normalized structure factors for **6** suggested a centric space group; this choice was confirmed by successful refinement.

The structure was solved by direct methods (MULTAN[66]); correct positions for non-hydrogen atoms were deduced from an E map. Hydrogen atoms were included as fixed contributors in idealized positions. The final least-squares refinement cycle (SHELX[67]) included independent positions and anisotropic thermal coefficients for all non-hydrogen atoms and a common isotropic thermal parameter for hydrogen atoms. The final difference Fourier map had no significant features. Atomic scattering factors and mass attenuation coefficients were taken from ref 68.

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Supplementary Material Available: Tables of atomic coordinations and thermal parameters for compound **6** (2 pages). Ordering information is given on any current masthead page.

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