

D_2 -Symmetric Dimer of 1,1'-Binaphthyl and Its Chiral π -Conjugated Carbodianion

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Abstract: The synthesis of a chiral, nonracemic π -conjugated system with D_2 point group of symmetry and the corresponding chiral carbodianion is described. Cu(II)-mediated oxidation of (*R*)-2,2'-dilithio-1,1'-binaphthyl (prepared from (*R*)(+)-2,2'-dibromo-1,1'-binaphthyl) gives the corresponding dimer, (*R*)(+)-**3**, which is a chiral π -conjugated derivative of *o*-tetraphenylene, a saddle shaped molecule. When partially resolved 2,2'-dibromo-1,1'-binaphthyl is used, amplification of the enantiomeric excess (ee) is observed in the coupling product (**3**). The dihedral angles between the naphthalene moieties in (*R*)(+)-**3** are about 70°, as determined by the X-ray crystallography. However, CD and UV spectra, and cyclic voltammetric data of (*R*)(+)-**3** are consistent with small, but far from negligible, conjugation (or homoconjugation) between the naphthalene moieties. The melting points of (*R*)(+)-**3** and its racemate differ by more than 200 °C. Reaction of (*R*)(+)-**3** with Li or Na in tetrahydrofuran (THF) gives the corresponding chiral carbodianions $3^{2-}, 2M^+$ ($M = \text{Li}$ and Na). NMR spectroscopy indicates two non-equivalent naphthalene moieties. UV-vis, ESR, NMR, and electrochemical studies show almost complete disproportionation of the radical anion to the carbodianion in THF with Na^+ as counterions. The free energy barrier for racemization in carbodianion $3^{2-}, 2\text{Na}^+$ is lowered by at least 25 kcal/mol compared to that in (*R*)(+)-**3**. However, carbodianions $3^{2-}, 2M^+$ ($M = \text{Li}$ and Na) remain configurationally stable at room temperature. Solid $3^{2-}, 2\text{Na}^+$ is a diamagnetic insulator.

Introduction

Chiral π -conjugated molecules and polymers continue to attract considerable attention because of their relevance to organic materials with interesting electronic properties.^{1–5} Such π -conjugated systems could also be useful for the enantioselective catalysis of electron-transfer reactions.⁶ High symmetry and configurational stability of the neutral chiral π -conjugated systems, as well as of the doped species and/or excited states, are important issues in many applications.

Chiral derivatives of *o*-tetraphenylene **1** (tetrabenzo[*a,c,e,g*]-cyclooctatetraene), a saddle shaped molecule, are among the most interesting targets.^{7–9} First, with adequate functionalization,

chiral derivatives of **1** may possess highly symmetric point groups (e.g., D_2),^{8,9} which are desirable both in catalysis and in the design of molecular solids. Second, these molecules may exhibit an extraordinarily high barrier for the ring inversion of the central cyclooctatetraene (COT) ring. For example, **2** was found to have a free energy barrier for racemization of 67 kcal/mol, compared to ~10 kcal/mol for the ring inversion in cyclooctatetraenes.^{10,11} As the dianion of cyclooctatetraene itself is a planar, aromatic compound,¹² the inversion barrier in these systems may be quite sensitive to the level of aromatic character

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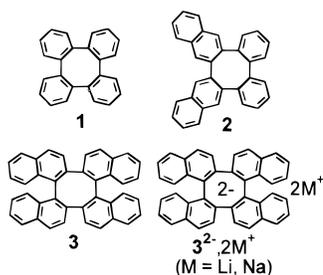
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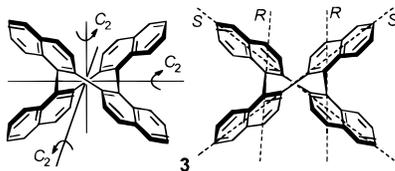
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that develops in the central COT ring upon n-doping. The study of suitable carbodians of chiral, nonracemic *o*-tetraphenylenes should provide key insights into this problem.



We design the chiral D_2 -symmetric *o*-tetraphenylene **3**, effectively a dimer of readily accessible chiral 2,2'-substituted-1,1'-binaphthyls. Both the high symmetry of chiral **3** and its synthesis have interesting stereochemical aspects.¹³

The parent *o*-tetraphenylene **1** is an achiral molecule belonging to the D_{2d} point group.¹⁴ In **1**, four chiral axes with the R, S, R, S labels can be defined along each of the four biphenyl CC bonds. The homochiral axes are orthogonal and interchangeable by the three orthogonal C_2 axes of symmetry. The heterochiral axes are interchangeable by the planes of symmetry. In derivatives of **1** with chiral π -conjugated system, the heterochiral axes are not interchangeable, but the homochiral axes may remain interchangeable. Thus, appropriately tetra- or di-substituted derivatives of **1** may provide configurationally rigid and symmetric (D_2 and C_2 point groups) chiral molecules.⁸



In **3**, three orthogonal C_2 axes of symmetry are compatible with the D_2 point group. One pair of the orthogonal chiral axes (e.g., *R,R*) corresponds to the two 1,1'-linkages and the other pair (e.g., *S,S*) corresponds to the two 2,2'-linkages of the naphthalene moieties. (Incidentally, it will be convenient to designate each enantiomer of **3** with only one *R/S* label, e.g., the one associated with the chiral axis of the 1,1'-linkage.) Therefore, the synthesis of **3** from 1,1'-binaphthyls must employ homochiral building blocks, analogously to the syntheses of derivatives of **1** from biaryls.⁸ By assuming that the 1,1'-binaphthyls are configurationally stable under the reaction conditions, the enantiomeric excess (ee) and the maximum yield of **3** will be nonlinear functions of the ee of the starting 1,1'-binaphthyl.¹⁵ This asymmetric amplification is analogous to that found in the duplication method, except that **3** (*R,R* and *S,S* products) and the (*R,S*)-product are different compounds.^{15,16}

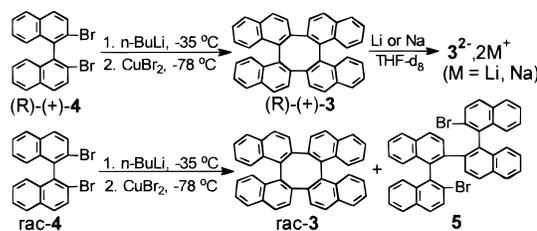
(13) In addition to the D_2 -symmetric **3**, other connectivities of four naphthalenes give *o*-tetraphenylenes with the D_{2d} , S_4 , C_4 , and C_2 (3 examples) point groups. The achiral D_{2d} compound is known (ref 7).

(14) X-ray structure for **1**: Irngartinger, H.; Reibel, W. R. K. *Acta Crystallogr.* **1980**, B37, 1724. (b) Average dihedral angles between the benzene rings in **1** are $62(2)^\circ$.

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Scheme 1



This article describes the synthesis and study of **3** and the corresponding carbodians **3²⁻,2M⁺** (M = Li and Na).

Results and Discussion

Dilithiation of (*R*)-2,2'-dibromo-1,1'-binaphthyl (**(R)-4**, 80–85% ee) with 2 equiv of *n*-BuLi at -30°C ^{17,18} is followed by the addition of CuBr₂ to give (*R*)-**3** in ~20% isolated yields (95+ % ee).^{19–21} Similar reactions starting from **rac-4** give very complex mixtures;^{17b} **rac-3** is isolated in 2–8% yields, in addition to the side product **5**, presumably with (*R,S*)-configuration at the 1,1'-binaphthyls (Scheme 1). Analogous side products and low isolated yields of tetraphenylenes were previously observed for coupling of racemic and configurationally stable (under the reaction conditions) biaryls to *o*-tetraphenylenes.⁸

In the HRMS (EI), the two most intense peaks correspond to (*M*/2)⁺ and *M*⁺. NMR spectra indicate that all four naphthalene moieties are equivalent.²² X-ray crystallography for (*R*)-**3**, which was synthesized from (*R*)-**4**, confirms the structure. The geometry of (*R*)-**3** resembles that of achiral **1**; that is, the naphthalene moieties are planar and their dihedral angles (1,1'-, 2,2', and diagonal) are in the $71\text{--}72^\circ$ range.^{14,23a} The molecular point group is approximately D_2 (Figure 1).^{23b}

UV–vis and CD spectra of (*R*)-**3** in CH₂Cl₂ are shown in Figure 2. As expected for the molecules with the dihedral angles of about 70° between the naphthalene chromophores, the UV–vis spectrum for (*R*)-**3** shows only a small bathochromic shift compared to that of naphthalene (see: the following paragraphs). The CD spectrum possesses four moderately intense Cotton effects, which may be grouped into two positive couplets (positive at long λ and negative at short λ Cotton effects) centered at 257 and 270 nm. The exciton coupling model in (*R*)-**3** would predict only one short-wavelength couplet, arising from two negative ((*R*)-1,1'-binaphthyls) and four positive ((*S*)-2,2'-, and (*S*)-diagonal-binaphthyls) exciton chiralities between four ¹B_g transitions of the naphthalene chromophores.^{24,25} The

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(22) One of the quaternary ¹³C resonances is unresolved in a ¹³C NMR spectrum.

(23) Mean planes: [C(1)–C(10)], rms deviation: 0.005 Å, max. dev.: 0.007 Å; [C(11)–C(20)], rms deviation: 0.017 Å, max. dev.: 0.033 Å. (b) Although there is only one crystallographic C_2 -axis, all four naphthalenes have essentially identical bond lengths and angles; e.g., rms deviation of D_2 equivalent bonds from their mean value is 0.004 Å.

(24) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy*; University Science Books: Mill Valley, California, 1983.

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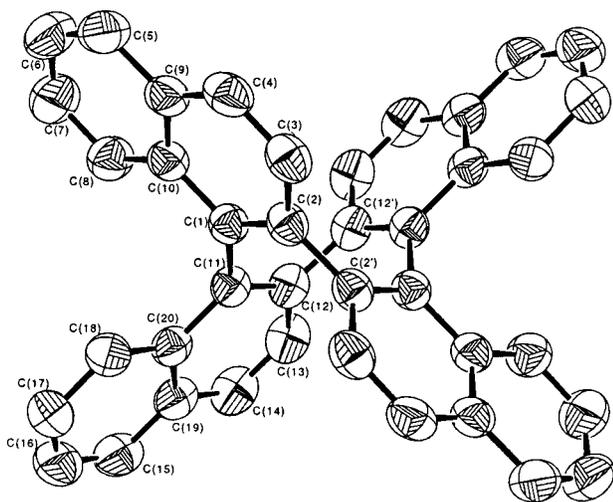


Figure 1. X-ray structure for **3**. The crystal was grown from a sample of (*R*)-**3** with +95% ee, but the absolute configuration was not established crystallographically. The disordered molecules of solvent of crystallization (acetonitrile) are not shown. Carbon atoms are depicted with ellipsoids representing 50% probability level.

presence of the additional intense long-wavelength couplet suggests that the interchromophoric conjugation or homoconjugation is not negligible in (*R*)-**3**.²⁶

For solid rac-**3** and (*R*)-**3**, IR spectra in the fingerprint regions are not superimposable, suggesting the presence of a racemic compound for the racemate.^{27,28a} The racemic compound of rac-**3** is unusually robust, as implied by the exceptional difference in melting points between the racemate (mp 428–430 °C) and the enantiomer (mp 213 °C).^{28b,29} The difference in melting points exceeding 200 °C would correspond to $-\Delta G^\circ$ of several kcal/mol for the free energy of formation of racemic compound from their crystalline enantiomers, according to the empirical relationship of Leclercq, Collet, and Jacques.^{28b,30} In the extensive compilation of thermodynamic data for racemates and the corresponding enantiomers, the most stable racemic compounds have $-\Delta G^\circ \approx 2$ kcal/mol (mp difference of ~ 75 °C).^{28c,30} We speculate that this unusually strong enantiomer discrimination in the solid **3** may be associated with the highly symmetric (*D*₂) saddle-like molecular shape.

Upon brief exposure of (*R*)-**3** in THF-*d*₈ to Li or Na metals, the ¹H NMR spectrum of the green to green/purple reaction mixture is broadened near the baseline. (For the reaction with Na, a strong ESR signal at $g \approx 2$ is observed for the reaction mixtures possessing a broad ¹H NMR spectrum.) Upon subsequent exposures to Li or Na, the reaction mixture turns purple, and a new set of resonances, corresponding to diamagnetic dianions of **3** (**3**²⁻, 2Li⁺ and **3**²⁻, 2Na⁺), appears. (In the case of Li metal, the experiment is complicated by precipitation of **3**²⁻, 2Li⁺.) The reaction with Na is stopped at the point where

(26) Analogous complex CD spectrum for a chiral tribenzotriptycene is interpreted in terms of homoconjugation between the three naphthalene chromophores: ref 24, pp 210–212. Harada, N.; Tamai, Y.; Takuma, Y.; Uda, H. *J. Am. Chem. Soc.* **1980**, *102*, 501. For a leading reference to limitations of simple exciton coupling model for CD spectra, see: Hattori, T.; Sakurai, K.; Koike, N.; Miyano, S. Goto, H.; Ishyia, F.; Harada, N. *J. Am. Chem. Soc.* **1998**, *120*, 9086.

(27) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*, Wiley: New York, 1994; Chapter 6.

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(29) Brock, C. P.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 9811.

(30) Leclercq, M.; Collet, A.; Jacques, J. *Tetrahedron* **1976**, *32*, 821.

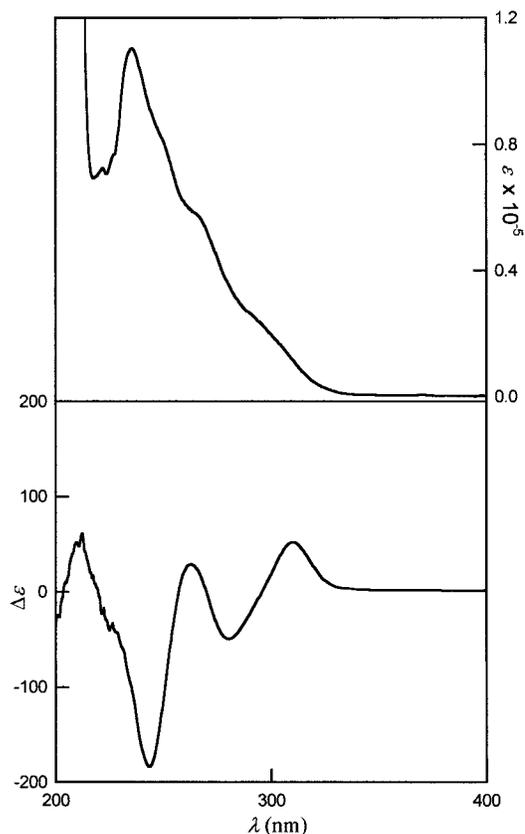


Figure 2. UV-vis (top) and CD spectra (bottom) for (*R*)-**3** in CH₂-Cl₂. UV-vis, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}} \times 10^{-5}$): 236 (1.1), 247S (0.86), 264S (0.57), 290S (0.26). CD, $\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon_{\text{max}}$): 244 (−184), 257 (0), 263 (+29), 270 (0), 281 (−50), 296 (0), 310 (+52).

the near maximum height of the ¹H resonances is attained. (The ESR signal at this point is essentially negligible.) For **3**²⁻, 2Na⁺, ¹H NMR spectra at ambient temperature lack resolved spin–spin couplings; at 328 K, the resonances of **3**²⁻, 2Na⁺ become even more broadened. At lower temperatures, ¹H and ¹³C NMR spectra for **3**²⁻, 2Na⁺ are better resolved and indicate two types of naphthalene moieties (Figure 3). Such symmetry breaking has been observed in the NMR spectra of carbodianions of **1**.³¹ It should be noted that analogous symmetry breaking in the corresponding radical ions of **1** has been associated with a strong ion pairing of the chelating aryl moieties with alkali metal ions.³²

Extended exposure to Na metal increases the line widths in the ¹H NMR spectrum of **3**²⁻, 2Na⁺ but no new peaks are discernible. Both the UV-vis spectra (vide versa) and iodine titrations (vide versa) of such overreduced **3**²⁻, 2Na⁺ are indistinguishable from those of **3**²⁻, 2Na⁺ with sharp NMR spectra. This indicates that the extent of overreduction of **3**²⁻, 2Na⁺ is very small. Carbodianion **3**²⁻, 2Na⁺ in THF-*d*₈ is quite persistent; it can be kept at −20 °C for two years or at 90 °C for 12 h in a flame sealed NMR tube, without detection of any extraneous resonances in the ¹H NMR spectrum.

The number of negative charge residing in the π -conjugated system of **3**²⁻, 2Na⁺ can be estimated from analysis of ¹³C chemical shifts and oxidative titration. For both **3** (in CDCl₃) and **3**²⁻, 2Na⁺ (in THF-*d*₈), one ¹³C resonance corresponding to the quaternary carbon is unresolved. Thus, calculation of negative charge assumes one spectral overlap and a negative charge in the −1.6 to −2.6 range is obtained.³³ The titration of

(31) Huber, W.; May, A.; Müllen, K. *Chem. Ber.* **1981**, *114*, 1318.

(32) Scholz, M.; Gescheidt, G. *J. Chem. Soc., Perkin Trans. 2* **1994**, 735.

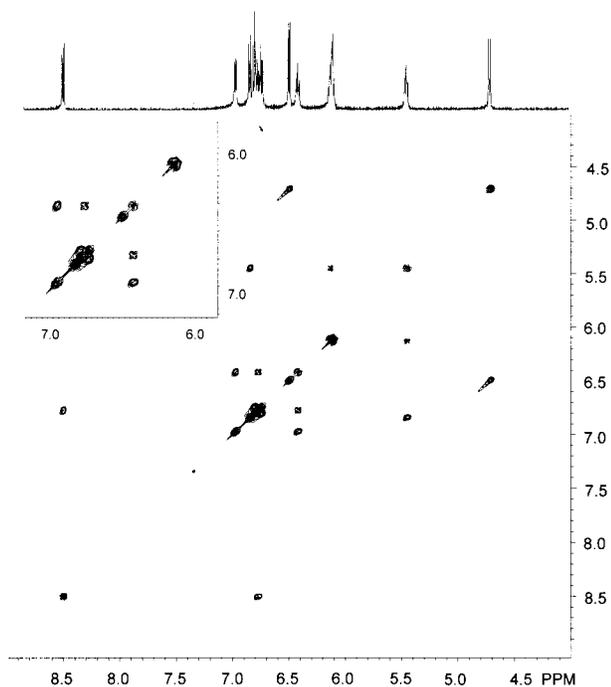


Figure 3. ^1H – ^1H COSY NMR (500 MHz, $\text{THF-}d_8$, 208 K) spectrum for dianion (*R*)- $\mathbf{3}^{2-}$, 2Na^+ . A sharp peak at 7.3 ppm is assigned to a small amount of benzene in the sample. The insert shows the region with two near-diagonal pairs of cross-peaks (6.815/6.750 and 6.139/6.113).

the NMR samples of $\mathbf{3}^{2-}$, 2Na^+ with iodine requires approximately 1 mol of I_2 for oxidation of 1 mol of $\mathbf{3}^{2-}$, 2Na^+ to the neutral $\mathbf{3}$. These analyses indicate that $\mathbf{3}^{2-}$, 2Na^+ in THF (or $\text{THF-}d_8$) is a carbidianion.

UV–vis spectra for $\mathbf{3}^{2-}$, 2Na^+ in THF consist of broad bands at $\lambda_{\text{max}} = 235$, 555, and 685 nm. Both $\mathbf{3}^{2-}$, 2Na^+ and (*R*)- $\mathbf{3}$ in THF have the band at $\lambda_{\text{max}} = 235$ nm with somewhat similar spectral envelopes. Naphthalene dianion (2Li^+) in ether possesses only a broad band at $\lambda_{\text{max}} = 530$ nm in the $\lambda = 350$ – 700 nm range.³⁴ The band at $\lambda_{\text{max}} = 685$ nm is rather broad, with more than half the absorbance of the band at $\lambda_{\text{max}} = 555$ nm, and consists of at least two broad peaks. The overall spectral envelope extends from about 650 to 780 nm at half-height. Thin-layers of (*R*)- $\mathbf{3}^{2-}$, 2Na^+ in $\text{THF-}d_8$ in flame sealed sample tubes, for which sharp NMR spectra and only background ESR signals are obtained, give reproducible UV–vis spectra in the $\lambda = 300$ – 800 nm region. Therefore, the long wavelength bands are undoubtedly associated with the diamagnetic dianion $\mathbf{3}^{2-}$, 2Na^+ . It should be noted that the longest wavelength band for a dianion of a “planarized” *o*-tetraphenylene is at $\lambda_{\text{max}} = 462$ nm.³⁵

It is instructive to compare the onsets of UV–vis absorption ($\sim 1/1000$ of the absorbance at λ_{max}) for the neutral (*R*)- $\mathbf{3}$ (340 nm), naphthalene in hexane (313 nm), 1,1′-binaphthyl in ethanol (333 nm), and 2,2′-binaphthyl in light petroleum (345 nm).³⁶ In conjunction with the results of CD spectroscopy (Figure 2), this suggests that the conjugation between naphthalene moieties is very small in $\mathbf{3}$, but not negligible.

Addition of small amounts of neutral (*R*)- $\mathbf{3}$ in THF to $\mathbf{3}^{2-}$, 2Na^+ in THF slightly lowers the bands at $\lambda_{\text{max}} = 685$ and

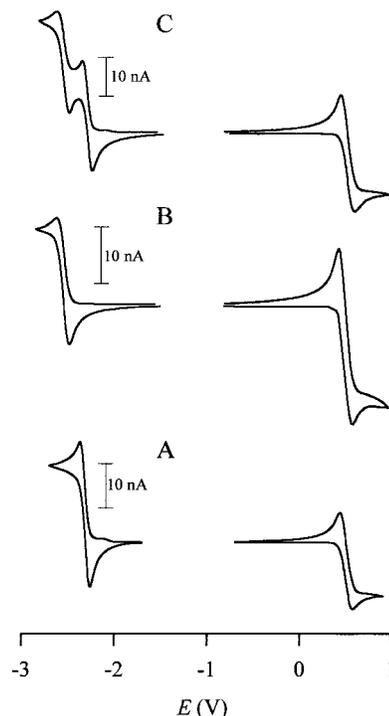


Figure 4. Cyclic voltammetry for (*R*)- $\mathbf{3}$ (trace A), naphthalene (trace B), and mixture naphthalene and (*R*)- $\mathbf{3}$ (trace C) in THF/TBAP at 100 mV/s. Scaling by 0.3 was used for currents of the reference ferrocene peaks (+0.510 V vs SCE).

555 nm (by dilution) and greatly increases the $\lambda_{\text{max}} = 235$ nm. Notably, no new bands are formed and the last band essentially coincides with the band at $\lambda_{\text{max}} = 235$ nm for (*R*)- $\mathbf{3}$ in THF. This suggests that the disproportionation in eq 1 is almost completely shifted from the side of radical anion to the side of the dianion and the neutral.



Cyclic voltammetry (CV) of $\mathbf{3}$ in THF/TBAP gives a single reversible wave at -2.31 V (with a small shoulder at -2.1 V), a significantly less negative potential than -2.57 V for naphthalene under the identical conditions (Figure 4). Thus, the CV results under the relatively less ion pairing, compared to those in $\mathbf{3}^{2-}$, 2Na^+ , are consistent (but not definitive) with only weak conjugation between the naphthalene moieties, disproportionation of the radical anion to the dianion, and negligible extent of further reduction of the dianion (with Na metal).

(*R*)- $\mathbf{3}^{2-}$, 2M^+ ($\text{M} = \text{Li}, \text{Na}$) in THF (or $\text{THF-}d_8$) and in the solid state can be handled at ambient or less than ambient temperature without any detectable racemization; that is, (*R*)- $\mathbf{3}$ with 95+ % ee is recovered from the iodine quenches/titrations of the carbidianions. At 90 °C, (*R*)- $\mathbf{3}^{2-}$, 2Na^+ in $\text{THF-}d_8$ racemizes with a half-life of 3.2 ± 0.9 h; that is, the recovered (*R*)- $\mathbf{3}$ has 83, 62, and 40% ee, after 1, 2, and 4 h, respectively. This corresponds to a barrier for the ring inversion, of $\Delta G^\ddagger = 28.9 \pm 0.4$ kcal/mol at 363 K. However, (*R*)- $\mathbf{3}$ can be kept under argon for 14.5 h at 340 °C with unchanged ee within an experimental error ($\pm 5\%$). This gives a lower limit to the barrier for the ring inversion of $\Delta G^\ddagger > 54$ kcal/mol at 613 K. This is a very conservative estimate; due to the additional steric crowding associated with the 1,1′-binaphthyl moieties in (*R*)- $\mathbf{3}$, the barrier for its ring inversion may even exceed $\Delta G^\ddagger = 67$ kcal/mol that was reported for $\mathbf{2}$.³⁷ Therefore, the barrier for the ring inversion in carbidianion (*R*)- $\mathbf{3}^{2-}$, 2Na^+ is lowered by at least 25 kcal/mol, and probably more than 40 kcal/mol,

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compared to the neutral (*R*)-**3**. The free energy difference between the barriers for racemization in (*R*)-**3** and (*R*)-**3**²⁻,2Na⁺ is unexpectedly large. It is unlikely, but not rigorously excluded, that the aromatic character of the negatively charged and "planarized" COT ring in the transition state for the ring inversion of the dianion plays a dominant role. Further detailed investigation is required in order to determine the mechanism for racemization in (*R*)-**3**²⁻,2Na⁺. Pathways involving the ring cleavage via bis(arylsodium),³⁸ as well as the role of ion pairing, radical anions, and radical trianions should be considered.

Magnetic studies of solids (*R*)-**3**^{*n*-},*n*M⁺ (*n* = 1–2, M = Na; *n* = 2, M = Li, Na) detect exclusively diamagnetic susceptibility in the 1.8–370 K temperature range. This is consistent with the studies in solution, indicating that the equilibrium in eq 1 is predominantly shifted to the diamagnetic dianion and neutral. In an alternative interpretation, the radical anions of **3** are present in the solid state and possess very strong intermolecular exchange antiferromagnetic coupling. Preliminary conductivity studies of (*R*)-**3**²⁻,2M⁺ (M = Li, Na) suggest a higher limit of 10⁻⁹ ohm⁻¹cm⁻¹ to conductivities in compressed powders. Thus, powders (*R*)-**3**²⁻,2M⁺ (M = Li, Na) are diamagnetic insulators.

Conclusions

o-Tetraphenylene derivative **3** provides chiral, nonracemic π -conjugated system with D₂ point group of symmetry. Both the neutral species and the corresponding carbodion are configurationally robust, although the free energy barrier for racemization in the carbodion is decreased at least 25 kcal/mol and probably by more than 40 kcal/mol compared to the neutral. Such an unexpectedly large free energy difference may not be exclusively associated with the aromaticity of the central COT ring in the dianion. This *o*-tetraphenylene system may provide a suitable framework for the construction of organic materials with configurationally stable, chiral π -conjugated systems, both neutral and n-doped. Saddle-shaped and highly symmetrical chiral *o*-tetraphenylene derivatives are promising candidates for robust enantiomer discrimination in the physical properties of crystals.

Experimental Section

General Procedures. Ether and tetrahydrofuran (THF) for use on the vacuum line were distilled from sodium/benzophenone under a nitrogen atmosphere. CuBr₂ was dried under vacuum at 70 °C overnight prior to use. Rac-, (*S*)-, and (*R*)-2,2'-dibromo-1,1'-binaphthyl (**4**) were prepared according to the literature procedures.¹⁷ Specific rotations for (*S*)- and (*R*)-**4** in pyridine at room temperature were in the 23–28 range; lit.¹⁷ [α]_D²⁵ = 33° (*c* = 1.00, pyridine). Ag(fod) was prepared as described by Wenzel, Bettes, Sadlowski, and Sievers.³⁹ Other major chemicals were obtained from Aldrich. Conventional double manifold vacuum lines (10⁻³ Torr), MBraun glovebox, and Vacuum Atmospheres glovebox were used. Column chromatography was carried out using TLC grade silica gel (Aldrich) and 10–20 psig pressure.

NMR spectra were obtained using Omega and Bruker spectrometers (¹H, 500 and 300 MHz) in CDCl₃ or THF-*d*₈. The chemical shift references were as follows: (¹H) TMS, 0.0 ppm (CDCl₃); THF-*d*₇, 3.58 ppm (THF-*d*₈); (¹³C) CDCl₃, 77.0 ppm (CDCl₃); THF-*d*₈, 67.45 ppm (THF-*d*₈). For selected spectra, exponential (EM) and Gaussian (GB) multiplication prior to the Fourier transform was employed. (The exponents were shown in Hz.)

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ESR spectra were acquired with a Bruker 200D X-band instrument at ambient temperature, using flame-sealed 5-mm o.d. CFQ tubes (Kontes).

IR spectra were obtained using the FT instrument Analect RFX-30 operating in ATR mode. A few drops of the compound in CH₂Cl₂ were applied to the surface of a ZnSe ATR plate parallelogram (45°, Wilmad), and after the solvent evaporated, the spectrum was acquired (32 scans, 2-cm⁻¹ resolution).

UV–vis absorption spectra were recorded at ambient temperature using the Perkin-Elmer Lambda 6 and the diode-array Hewlett-Packard 8450A (HP 8450A) spectrophotometers. The sample chamber of the Perkin-Elmer spectrophotometer was accessible from a Vacuum Atmospheres glovebox. The spectra (λ = 200–900 nm) were obtained using modified 2-mm path length quartz cells, equipped with high-vacuum PTFE stopcocks (Kontes). The HP 8450A spectrophotometer was used to obtain spectra of the thin films of (*R*)-**3**²⁻,2Na⁺/THF-*d*₈, contained in the flame-sealed 5-mm o.d. ESR (quartz) or NMR (Pyrex) tubes (λ = ~300–800 nm) and to obtain data for the Lambert–Beer plot for 2–8 μ M (*R*)-**3** in CH₂Cl₂ (6 concentrations, *R* = 0.999 at λ_{max} = 236 nm, 10-mm path length quartz cells).

Concurrent UV–vis and CD spectra for 5–14 μ M (*R*)-**3** in CH₂Cl₂ at 24 °C were obtained using Applied Photophysics Pistar 180 CDF Spectrometer at the University of North Carolina Macromolecular Interactions Facility.

Cyclic voltammograms were recorded using PARC 270 electrochemistry system, Pt-disk (100- μ m diameter) working electrode, THF/TBAP (TBAP = tetrabutylammonium perchlorate) at ambient temperature in a Vacuum Atmospheres glovebox. Ferrocene (0.510 V vs SCE) was used as a reference. Naphthalene was transferred to the glovebox in a Schlenk vessel. Peak-to-peak potentials were 100 mV and 140 mV for (*R*)-**3** and naphthalene, respectively (scan rates of 50–100 mV/s).

Optical rotations were measured with Autopol III (Rudolph Research) at ambient temperature.

Elemental analyses were carried out by M-H-W Laboratories, P.O. Box 15149, Phoenix, AZ 85060.

¹H NMR Spectra with Chiral Shift Reagents. The spectrum for racemate (2–4 mg) in CDCl₃ (0.4–0.5 mL) was first obtained; then, Ag(fod) and ytterbium tris[3-(heptafluoropropyl)hydroxymethylene]-(+)-camphorate] (Yb(hfpc)) were added until baseline separation between enantiomers in one of the multiplets was attained. Typically, approximately equal amounts (by weight) of **3**, Ag(fod), and Yb(hfpc) gave the optimum tradeoff between dispersion and line width. (**4** required more shift reagents.) Similar conditions were employed for determinations of the ee in nonracemic **3** and **4**. In a typical experiment for **3**, each of the two doublets at 6.973 and 7.530 ppm, was shifted downfield and split into a pair of doublets at 7.046, 7.095 and 7.573, 7.594, respectively. (The downfield-shifted doublets corresponded to (*R*)(+)-**3**.) For selected spectra, Gaussian/Lorentzian numerical fits were carried out using NUTS software. The experimental errors in determination of ee were estimated at 5 and 1% for ee's near 100 and 0%, respectively.

X-ray Crystallography. A Siemens P4 automatic diffractometer was used to collect the data. Colorless, tabular crystals of (*R*)(+)-**3** were obtained from acetonitrile solution by slow evaporation. Crystal data for (*R*)(+)-**3**, containing a disordered molecule of acetonitrile, were as follows: C₄₂H₂₇N, *M* = 545.65, monoclinic, *a* = 18.158(3) Å, *b* = 9.0659(13) Å, *c* = 9.6297(11) Å, β = 92.140(10)°, *V* = 1584.1(4) Å³, *T* = 293(2) K, space group C₂, *Z* = 2, Mo K α (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares on *F*². A total of 2687 reflections were observed, and 2012 reflections with *I* > 2 σ (*I*) were recorded. Refinement statistics with 252 parameters were as follows: *wR* = 0.1183 (*I* > 2 σ (*I*)), *R* = 0.0456 (*I* > 2 σ (*I*)), GOF = 1.012. Flack parameter of -3(10) indicated that the absolute configuration was uncertain from this set of crystallographic data.

Synthesis of (*R*)(+)-3**.** *n*-BuLi (9.7 mL of a 2.5 M solution in hexane, 24.3 mmol) was added to a solution of (*R*)(+)-2,2'-dibromo-1,1'-binaphthyl (4.00 g, 9.71 mmol, 80% ee) in ether (400 mL) at -35 °C. After stirring for 2 h, the reaction mixture was cooled with -78 °C bath, and then, CuBr₂ (13.0 g, 58.2 mmol) was added. The reaction

mixture was allowed to attain ambient temperature over a 12-h period, and then cold water was added to the reaction mixture. The organic layer was washed with HCl, water, and Na₂CO₃, and the solution was dried over MgSO₄. Concentration in vacuo afforded 3.173 g of a crude product. Analogous reaction, starting from 2,2'-dibromo-1,1'-binaphthyl (3.34 g, 8.11 mmol, ~85% ee) gave 2.65 g of similar crude product. The crude products were combined and purified three times by column chromatography (silica gel of TLC grade, hexane/chloroform, 3:1) to give white powder (1.00 g, 22% yield, 95+ % ee) with mp 213 °C and $[\alpha]_D^{25} +430^\circ$ ($c = 0.0115$, chloroform). In another reaction, (*R*)-(+)-**4** (0.40 g, 78% ee) gave (*R*)-**3** (39.3 mg, 90% ee) in 16% yield, after column chromatography and recrystallization (EtOH/hexane, 1:1). Anal. Calcd for C₄₀H₂₄: C, 95.21; H, 4.79. Found: C, 94.70; H, 4.96. HR EIMS (200 °C), *m/z* (ion type, % RA for *m/z* 50–510, deviation for the formula): 505.1916 ((*M* + 1)⁺, 40%, 0.9 ppm for ¹²C₃₉13C₁-1H₂₄), 504.1868 (M⁺, 93%, -1.9 ppm for ¹²C₄₀1H₂₄), 252.0943 ((*M* / 2)⁺, 100%, 1.7 ppm for ¹²C₂₀1H₁₂). ¹H NMR (500 MHz, CDCl₃, ¹H-¹H COSY cross-peaks) 7.748, 7.745 (d and d, 1:1, *J* = 8.5, *J* = 8.5, 8 H, 7.530, 7.319, 7.136 (weak), 6.971 (weak)), 7.530 (d, *J* = 8.5, 4 H, 7.748), 7.319 (t, *J* ≈ 8, 4 H, 7.745, 7.136, 6.971 (weak)), 7.136 (t, *J* ≈ 8, 4 H, 7.319, 6.971), 6.971 (d, *J* = 8.5, 4 H, 7.136, 7.319 (weak), 7.745 (weak)). ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃) aromatic quaternary region, expected, 4 resonances; found, 3 resonances at 140.6 (q), 135.5 (q), 132.3 (q); aromatic non-quaternary region, expected, 6 resonances; found, 6 resonances at 127.85, 127.78, 127.0, 126.22, 126.10, 125.3. IR (cm⁻¹) 3051 (Ar-H), 1592 (Ar).

Rac-3. *n*-BuLi (4.60 mL of 2.5 M solution in hexane, 11.5 mmol) was added to a solution of 2,2'-dibromo-1,1'-binaphthyl (1.60 g, 3.89 mmol) in ether (160 mL) at -35 °C. After 2 h, CuBr₂ (5.21 g, 23.3 mmol) was added as solid under nitrogen flow at -78 °C. The reaction mixture was allowed to warm to ambient temperature overnight and, then, quenched with water (100 mL). After extraction with ether (3 × 100 mL), the combined organic layer was washed with 5% HCl (100 mL), dilute NaHCO₃, and water (2 × 100 mL). The water layer from washing was extracted with ether (50 mL), and then the combined organic layer was dried over MgSO₄. Concentration in vacuo gave 1.65 g of brown viscous solid. Column chromatography (TLC grade silica gel, 5–20% chloroform in hexane) gave two fractions: F1 (less polar), 0.103 g (8%) and F2 (more polar), 0.232 g.

F1: 5, light yellow powder, mp 282–284 °C. EIMS cluster: *m/z* (% RA for *m/z* = 300–800) at (*M* - 2Br)⁺: 504.4 (100); at (*M* - Br)⁺: 585.3 (38) at M⁺: 664.2 (37); *m/z* (% RA for *m/z* = 660–670) at M⁺: 662 (48), 663 (22), 664.2 (100), 665 (42), 666.3 (56), 667 (23); calcd for C₄₀H₂₄Br₂: 662.0 (48), 663.0 (21), 664.0 (100), 665.0 (43), 666.0 (55), 667.0 (22). HR EIMS, *m/z* (ion type, % RA, deviation for the formula): 662.0244 (M⁺, 50%, 0.1 ppm for ¹²C₄₀1H₂₄79Br₂), 664.0227 (M + 2)⁺, 100%, 0.4 ppm for ¹²C₄₀1H₂₄79Br₁81Br₁), 666.0217 (M + 4)⁺, 50%, 2.0 ppm for ¹²C₄₀1H₂₄81Br₂). ¹H NMR (500 MHz, CDCl₃): 293 K, 7.969 (d, *J* = 8, 2 H), 7.799 (d, *J* = 9, 2 H), 7.789 (d, *J* = 8, 2 H), 7.636 (d, *J* = 9, 2 H), 7.565 (d, *J* = 9, 2 H), 7.535 (d, *J* = 8, 2 H), 7.333 (t, *J* = 7, 2 H), 7.182 (t, *J* = 7, 2 H), 7.053 (t, *J* = 8, 2 H), 6.758 (br t, *J* = 7, 2 H), 6.604 (d, *J* = 8, 2 H), 6.420 (br, 2 H). ¹H NMR (500 MHz, CDCl₃, ¹H-¹H COSY cross-peaks): 328 K, 7.961 (d, *J* = 8, 2 H, 7.783), 7.783 (d, *J* = 9, 2 H, 7.961); 7.773 (d, *J* = 8, 2 H, 7.315), 7.315 (t, *J* = 8, 2 H, 7.773, 7.036), 7.036 (t, *J* = 8, 2 H, 7.315, 6.597), 6.597 (d, *J* = 9, 2 H, 7.036); 7.623 (d, *J* = 9, 2H, 7.543), 7.543 (d, *J* = 9, 2 H, 7.623); 7.517 (d, *J* = 8, 2 H, 7.157), 7.157 (t, *J* = 7, 2H, 7.517, 6.725), 6.725 (t, *J* = 8, 2 H, 7.157, 6.402), 6.402 (d, *J* = 8, 2 H, 6.725). ¹³C{¹H} DEPT (135°) NMR (125 MHz, CDCl₃): 293 K, aromatic quaternary region, expected, 8 resonances; found, 8 resonances at 137.9 (q), 136.9 (q), 135.0 (q), 134.5 (q), 132.6 (q), 132.4 (q), 131.8 (q), 124.7 (q); aromatic non-quaternary region, expected, 12 resonances; found, 12 resonances at 130.2, 129.60, 129.53, 127.69, 127.64, 127.2, 127.0, 126.6, 126.4, 126.1, 125.8, 125.6. IR (cm⁻¹): 3057 (Ar-H), 1581 (Ar).

F2: rac-**3**, fractionation by column chromatography (10% chloroform in hexane) gave white crystal (0.054 g, 6%); crystallization of the first fraction in 1:1 hexane/ethanol gave 0.038 g (4%) of white powder (mp 428–430 °C (under argon)). In another reaction, rac-**4** (0.40 g) gave rac-**3** (18.5 mg) in 8% yield, after column chromatography and recrystallization. FAB MS (3-NBA) cluster: *m/z* (% RA for *m/z* =

480–1500) at M⁺: 504.2 (100), 505.2 (70), 506.2 (25). ¹H NMR (500 MHz, CDCl₃): 7.749 (d, *J* = 8, 8 H), 7.530 (d, *J* = 8, 4 H), 7.318 (t, *J* = 8, 4 H), 7.136 (t, *J* = 8, 4 H), 6.973 (d, *J* = 8, 4 H). IR (cm⁻¹): 3052 (Ar-H), 1594 (Ar).

(*R*)-3²⁻,2M⁺ (M = Li, Na): Preparation and Magnetic Resonance Spectroscopy. (*R*)(+)-**3** (1.5–11 mg) was evacuated overnight in a 5-mm NMR or ESR tube equipped with a high-vacuum PTFE stopcock. The tube was moved to an argon-filled Vacuum Atmospheres glovebox, where a freshly cut piece of Na (or Li) metal (multimolar excess) was spread on the surface of the upper part of the tube (or suspended). After the tube was evacuated overnight, THF-*d*₈ (~0.4 mL) was vacuum transferred from purple sodium/benzophenone. The tube was flame-sealed, and the NMR spectrum of (*R*)(+)-**3** was immediately recorded. ¹H NMR (500 MHz, THF-*d*₈): 293 K, 7.760 (t, *J* = 9, 8 H), 7.534 (d, *J* = 8, 4 H), 7.283 (t, *J* = 8, 4 H), 7.100 (t, *J* = 8, 4 H), 6.938 (d, *J* = 9, 4 H). Initial brief exposure (a few seconds) of the reaction mixture to alkali metal gave the light green color, followed by the purple color after subsequent exposures to the alkali metal. These color changes for the reaction with Na were studied both with ESR and NMR spectroscopies on the same sample: ESR, featureless, broad peak at *g* ≈ 2 increasing in intensity)

As the reaction continued for a few minutes, the color became more intense, and ¹H NMR spectra were recorded in 10–20 s intervals. The reaction mixture was kept in contact with the surface of the metal, until the maximum height for the resonances of the product was attained or, in the case of reaction with Li, until the product precipitated in the NMR tube.

(*R*)-3²⁻,2Li⁺: ¹H NMR (500 MHz, THF-*d*₈): 293 K, 8.47 (br, 2H), 7.0–6.4 (br m, 12H), 6.25 (br, 2H), 6.12 (br, 4H), 5.56 (br, 2H), 4.85 (br, 2H).

(*R*)-3²⁻,2Na⁺: ¹H NMR (500 MHz, THF-*d*₈): 293 K, 8.52 (br, 2H), 7.07 (br, 2H), 6.87 (br, 8H), 6.57 (br, 4H), 6.19 (br, 4H), 5.48 (br, 2H), 4.79 (br, 2H). ¹H NMR (500 MHz, THF-*d*₈, GB = +0.85, EM = -1.9, ¹H-¹H COSY cross-peaks in aromatic region): 208 K, 8.513 (d, *J* = 8, 2H, 6.786), 6.786 (t, *J* ≈ 8, 2H, 8.513, 6.426), 6.426 (t, *J* = 7, 2H, 6.786, 6.982), 6.982 (d, *J* = 7, 2H, 6.426); 6.503 (d, *J* = 7, 2H, 4.720), 4.720 (d, *J* = 7, 2H, 6.503); 6.854 (d, *J* = 7, 2H, 5.460), 5.460 (t, *J* = 7, 2H, 6.854, 6.139), 6.139 (t, *J* ≈ 7, 2H, 5.460, 6.113), 6.113 (d, *J* = 8, 2H, 6.139); 6.815 (d, *J* = 8, 2H, 6.750, AB), 6.750 (d, *J* = 8, 2H, 6.815, AB). ¹³C{¹H} DEPT (135°) NMR (125 MHz, THF-*d*₈, EM = +3 Hz): 223 K, aromatic quaternary region, expected, 8 resonances; found, 7 resonances at 142.0 (q), 141.8 (q), 141.4 (q), 135.5 (q), 132.1 (q), 110.0 (q), 72.6 (q); aromatic non-quaternary region, expected, 12 resonances; found, 12 resonances at 128.6, 128.4, 127.5, 125.9, 125.6, 124.68, 124.58, 119.4, 118.6, 118.0, 111.0, 84.2. ¹³C{¹H} DEPT (135°) NMR (125 MHz, THF-*d*₈, EM = +3 Hz): 208 K, aromatic quaternary region, expected, 8 resonances; found, 7 resonances at 141.8 (q), 141.6 (q), 141.3 (q), 135.5 (q), 131.6 (q), 110.1 (q), 72.4 (q); aromatic non-quaternary region, expected, 12 resonances; found, 12 resonances at 129.0, 128.6, 127.4, 125.54, 125.46, 124.6, 124.3, 119.3, 118.6, 117.3, 111.3, 84.9.

(*R*)-3²⁻,2Na⁺: UV-vis Spectroscopy. (*R*)-3²⁻,2Na⁺ in THF-*d*₈ (from an NMR tube) was diluted with THF or prepared separately in the glovebox by stirring (*R*)(+)-**3** with Na metal (excess) in THF overnight. (The inner surfaces of quartzware and glassware were washed with dilute solution of (*R*)-3²⁻,2Na⁺ immediately prior to the experiments, to remove trace amounts of moisture and oxygen.)³⁵ When (*R*)-**3** in THF was added to the above dilute solution of (*R*)-3²⁻,2Na⁺, neither change in color nor change in the absorption spectrum (besides dilution effect) were observed.

In another set of experiments, NMR and ESR samples of 0.01–0.03 M (*R*)-3²⁻,2Na⁺ in THF-*d*₈ (in flame sealed 5-mm o.d. tubes) were directly used to obtain UV-vis spectra on a diode array instrument. Spectra of a thin layer of the solution on the wall of the tube were recorded.

Magnetic Studies of Solid (*R*)-3ⁿ⁻,nM⁺ (n = 1–2, M = Li, Na). All solid samples for magnetic measurements were prepared in flame-sealed, special design, quartz tube made from the EPR-quality 5-mm OD (200-mm long) tubing with thin quartz bottom about 60 mm from the end of the tube. In each case, THF or THF-*d*₈ was removed under

vacuum (10⁻³ Torr), and partial pressure of helium gas was introduced for a good thermal contact.

Solids (R)-3²⁻,2Li⁺ were prepared from (R)-3 and Li metal in a glovebox. Solids (R)-3²⁻,2Na⁺ were obtained similarly to their Li-counterparts or by removal of solvent from NMR samples, or by using the following procedure.

The reaction vessel had a reaction compartment (A), which was connected via coarse glass frit to the quartz tube (B). (The quartz tube is described in the preceding paragraphs.) The empty vessel was evacuated at 180–200 °C overnight. In one set of experiments a single portion of (R)(+)-3 (4–5 mg) was loaded to the part A. In another set of experiments, (R)(+)-3 (4–5 mg) was loaded to the part A and the quartz tube (part B); the A/B ratios were from 1/1 to 3/1. The magnetic stirring bar was loaded to the part A. The vessel was then evacuated and flushed with argon. Subsequently, a freshly cut piece of Na was added to part A in an argon-filled Vacuum Atmospheres glovebox. The vessel was connected to the vacuum line, the stopcock was evacuated for 10 h, and, then, THF (~0.3 mL) was vacuum transferred. Initial stirring of the reaction mixture produced the green color, followed by the purple color. After 24 h of stirring, the purple reaction mixture was filtered to the quartz tube (and mixed with remaining (R)(+)-3, where applicable). Subsequently, THF was removed under vacuum and the reaction mixture was evacuated overnight. The partial pressure of helium was introduced and the quartz tube was flame sealed for storage in liquid nitrogen.

Magnetic measurements (1.8–370 K, 20–50000 Oe) revealed negative magnetic moment (diamagnetic) for all samples studied. After the first set measurements, selected samples were exposed to air. Although, the purple color disappeared rapidly, the magnetic moment remained essentially the same, further confirming diamagnetism.

Electrical Conductivity Studies of Solid (R)-3²⁻,2M⁺ (M = Li, Na). The solid samples were prepared as described above. The resistance was measured for the compressed powders. For the two-probe measurements, a simple apparatus of Wudl and Bryce,⁴⁰ connected to a Keithley DMM196, was employed. For the four-probe measurements, carbanion was compressed with IR press (~6 ton) onto Teflon template with four niobium electrodes in a square (5 × 5 mm) configuration in a glovebox. The resistance was measured with the computer-controlled setup with current source (Keithley 220), switch box (Keithley 7001) and Keithley DMM196.

(R)-3²⁻,2M⁺ (M = Li, Na): Quenching and Titration of with Iodine. Solutions of (R)-3²⁻,2M⁺ (M = Li, Na) in THF (or THF-*d*₈) were quenched with excess of I₂ in THF following selected NMR, UV-vis, and magnetic measurements. NMR samples of 3²⁻,2Na⁺, prepared from ≥ 5 mg of 3, were used for titrations. A sharp color change, corresponding to the charge between -1.7 and -1.8, was observed. After the usual workup, 3 was recovered in >90% yield. For all cases, where (R)-3²⁻,2M⁺ (M = Li, Na) was handled and stored at room temperature or below, (R)(+)-3 was recovered with unchanged ee within experimental error (± 5%, for the near 100% ee samples). This includes

a sample of (R)-3²⁻,2Na⁺ in THF-*d*₈ stored in a refrigerator at approximately -20 °C for 2 years.

Racemization Experiments on (R)(+)-3 and (R)-3²⁻,2Na⁺. (R)(+)-3 (~2 mg) was placed in a short melting point capillary, which was flame-sealed under argon and then heated for 14.5 h at 340 °C in a melting-point apparatus. The brown solid at the bottom of the tube was dissolved in CDCl₃. ¹H NMR (CDCl₃, chiral shift reagents) spectrum indicated pure (R)(+)-3 with unchanged ee within experimental error (±5%, for the near 100% ee samples). This corresponds to a lower limit to ring inversion at 613 K, of Δ*G*[‡] > 54 kcal/mol.

NMR tubes containing (R)-3²⁻,2Na⁺ in THF-*d*₈ (each prepared from ~2 mg of (R)(+)-3) were placed in an oil bath kept at 90 ± 3 °C for *t* = 1, 2, and 4 h. Following the heating, ¹H NMR spectra of 3²⁻,2Na⁺ showed only minor changes in line widths; the integrations for resonances of 3²⁻,2Na⁺ vs the residual solvent peaks of THF-*d*₇ were 80, 70, and 110%, respectively, of the original values before heating. The I₂-titrations gave the charges of -1.6, -1.7, and -1.6, respectively. After the usual workup, ¹H NMR (CDCl₃, chiral shift reagents) spectra of 3 showed 83, 62, and 40% ee, respectively. The rate constants (*k*) were calculated from the following equation, ln[1/(2*x* - 1)] = 2*kt*, where *x* is the fraction of the (R)-enantiomer, assuming reversible first-order reactions;⁴¹ then, at half-life (*t* = τ), *x* = 3/4 and τ = ln 2/2*k*. The free energy barriers for ring inversion at 363 K, calculated from the Eyring equation, were 29.01, 28.83, and 28.86 kcal/mol, respectively. When the uncertainties in temperature (±3 °C) and in ee determinations from NMR integrations (±5%) were included, Δ*G*[‡] = 28.9 ± 0.4 kcal/mol and τ = 3.2 ± 0.9 h were obtained. In an analogous experiment, nearly racemic 3 was obtained (ee ≈ 3%) after 12 h at about 90 °C.

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Supporting Information Available: Selected ¹H and/or ¹³C NMR spectra ((R)-3, 5), ¹H NMR spectra with chiral shift reagents for rac-3 and (R)-3, IR spectra ((R)-3 and rac-3), selected ¹H, ¹³C NMR, ESR, and UV-vis spectra for (R)-3²⁻,2Na⁺ and its generation (Figures 1s–15s) (PDF). An X-ray crystallographic file (CIF) for 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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