

## Use of benzene rings as parts of rigid rotors: dynamic stereochemistry of 9-(aryl-X)tritycene derivatives

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**Abstract** - Dynamic stereochemistry of 9-benzyltritycene, 9-phenoxytritycene, and their various derivatives, which behave as molecular bevel gears with a two-toothed wheel and a three-toothed one, were studied by dynamic  $^1\text{H}$  and/or  $^{13}\text{C}$  NMR spectroscopy and molecular mechanics calculations.

### INTRODUCTION

The phenyl group as well as its substituted derivatives has been used as a two-fold rotor in the studies of dynamic stereochemistry of structurally interesting molecules such as molecular propellers because of the rigid and planar structure (ref. 1). Triptycene has a unique structure in which three benzene rings are three-dimensionally arranged and the 9-tritycyl (Tp) group constitutes a rigid three-fold rotor with a high rotational barrier. Di-9-tritycyl compounds of the type  $\text{Tp}_2\text{X}$  ( $\text{X}=\text{CH}_2$ , O, etc.) have been shown to behave as dynamic gears with very low energy barriers ( $< 4 \text{ kcal mol}^{-1}$ ) to gearing and high barriers ( $30\text{--}40 \text{ kcal mol}^{-1}$ ) to "slippage" of the gear (ref. 2).

We have been interested in the dynamic stereochemistry of 9-benzyltritycene (1), 9-phenoxytritycene (2) and their derivatives ( $\text{Ph-X-Tp}$ :  $\text{X}=\text{CH}_2$ , O), in which a two-fold rotor (Ph) and a three-fold rotor (Tp) are attached to a central atom X. Therefore, these molecules are regarded to constitute bevel gear systems with a two-toothed wheel and a three-toothed one. At the early stage of this research a variety of substituted derivatives of 1 and 2 were studied by  $^1\text{H}$  NMR of low magnetic field (ref. 3). Thereafter high-field NMR spectrometers have become available and this prompted us to re-investigate this field in a more sophisticated way. We made  $^1\text{H}$  and  $^{13}\text{C}$  dynamic NMR studies and molecular mechanics calculations on several selected compounds including the parent compounds 1 and 2, which has revealed some new aspects that were not disclosed in the earlier studies. Recent advances are described in this article together with some of the early results.

### 9-BENZYLTRITYCENE AND 9-PHENOXYTRITYCENE

These compounds exist in a conformation in which the Ph group is coplanar with the Tp-X bond and is flanked by two benzene rings of the Tp moiety as shown by the Newman projection along

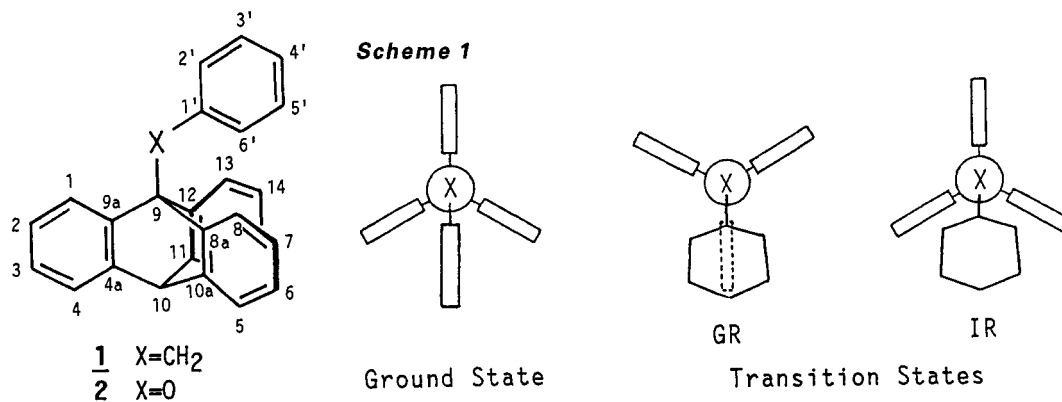


TABLE 1. Kinetic parameters for 1 by dynamic NMR.

Obs'd Carbon	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G_{250}^\ddagger$
	kcal mol <sup>-1</sup>	cal mol <sup>-1</sup> K <sup>-1</sup>	kcal mol <sup>-1</sup>
4a/10a/11	10.0 ± 0.4	-3.5 ± 1.6	10.8
3'/5'	8.5 ± 0.1	-2.6 ± 0.2	9.2

TABLE 2. Relative steric energies by BIGSTRN-3 calculations (kcal mol<sup>-1</sup>).

Stationary Point	1	2
	GS	0
TS / GR	11.91	7.79
TS / IR	10.30	14.91

the Tp-X axis in Scheme 1, thus constituting a static bevel gear system. Two fundamental processes of molecular motions are to be considered: one is gear rotation (GR) in which concomitant rotation of the Tp-X bond by 120° and the Ph-X bond by 180° occurs in a disrotatory fashion and the other is isolated rotation (IR) of the Ph-X bond without rotation of the Tp-X bond. Transition states of these processes are also schematically shown by Newman projections in Scheme 1. Isolated rotation of the Tp moiety may be neglected because the plausible transition state, in which the Ph group and one of the benzene rings of the Tp skeleton becomes coplanar, is highly unlikely.

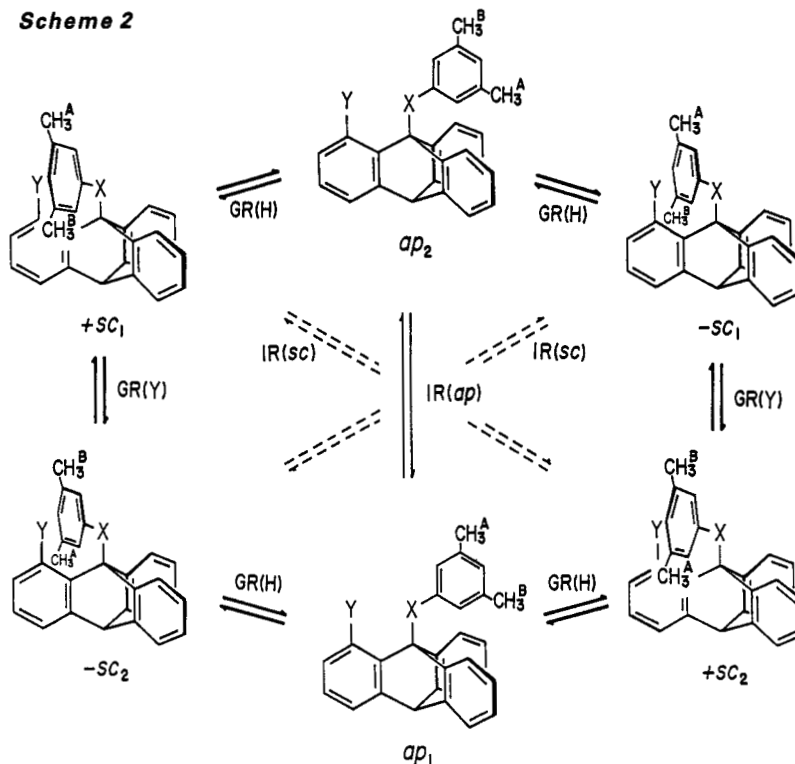
The <sup>13</sup>C NMR spectra of 1 and 2 at ambient temperature reflect the fast internal motions of the molecules and comprise ten aromatic carbon signals together with three and two aliphatic carbon signals for 1 and 2, respectively (ref. 5). On lowering the temperature, all the aromatic carbon signals in 1 except for those of the ipso- and p-carbons of the Ph group broadens and each of them splits into two peaks. A nearly "frozen" spectrum is obtained at -102 °C. Each of the aromatic carbons of the Tp moiety gives rise to two peaks with an intensity ratio of 2:1 while the o- and m-carbons of the Ph group afford two equally intense peaks, respectively. Lineshape analyses were made for the 4a/10a/11-C and 3'/5'-C signals, which gave kinetic parameters for the Tp-C and Ph-C rotations, respectively, as shown in Table 1. The Tp-C rotation entirely occurs by the GR process, while the Ph-C rotation occurs by either GR, IR or both, as discussed above. The results that the Ph-C rotation has a considerably lower barrier than the Tp-C rotation indicate that the Ph-C rotation mainly occurs by the IR process. Actually the Ph-C and Tp-C rotations have rate constants of 1300 and 25 s<sup>-1</sup>, respectively, at -65 °C, and thus the kinetic parameters for the Ph-C rotation can be regarded as those for the IR process.

In compound 2, internal motions are still fast on the NMR time scale even at -111 °C, the lowest attainable temperature, although some of the peaks are considerably broadened. Analysis of the broadened signals allowed a quite rough estimate that the Tp-O rotation and the Ph-O rotation have nearly the same energy barriers of ca. 7 kcal mol<sup>-1</sup>.

In order to supplement the experimental results, we made molecular mechanics calculations on 1 and 2 using the BIGSTRN-3 program with a modified MM2 force field. [The BIGSTRN-3 calculation on 1 with the original MM2 force field has been done by Mislow and his coworkers (ref. 6).] A ground-state conformation and transition-state conformations corresponding to GR and IR were obtained as stationary points for each compound. The relative steric energies of these points are shown in Table 2. As for 1, the calculated barriers to the GR and IR processes are comparable to the experimentally obtained ones, although somewhat over-estimated. The IR barrier of 2 was calculated to be far higher than the GR barrier. This suggests that the Ph-O rotation should occur by the GR process, supporting the estimation from experiments.

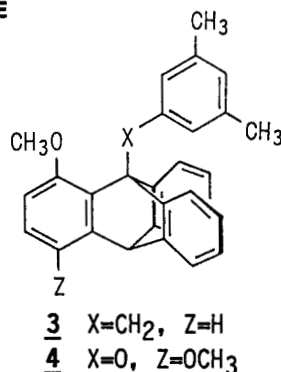
It is therefore concluded that 9-phenoxytriptycene (2) behaves as a well-meshed dynamic bevel gear, while in 9-benzyltriptycene (1) "slippage" of the gear is a more favorable process than the dynamic gearing. This difference is understood in terms of two factors: valencies (tetraivalent for C and divalent for O) and bond lengths (1.49-1.55 Å for C-C and 1.36-1.42 Å for C-O). In the GR transition state of 1, there exist eclipsing interactions between methylene hydrogens and the peri-hydrogens of the triptycene moiety, while in 2 such interactions involving the lone pair electrons might be negligible. This valency effect may be predominant over the bond-length effect resulting in the higher GR barrier in 1 than in 2. Meanwhile the bond-length effect dominates in determining the IR barrier: shorter C-O bonds increase the steric interaction between the ortho hydrogens of the Ph group and the peri-hydrogens of the Tp moiety in the IR transition state resulting in the higher IR barrier in 2 than in 1.

Scheme 2



## PERI-SUBSTITUTED 9-(3,5-DIMETHYLBENZYL)TRIPTYCENE

Introduction of a substituent at a peri-position of the Tp moiety complicates the modes of internal motions as shown in Scheme 2. Two *m*-methyl groups in the Ph moiety are introduced so that the molecular motions can be monitored by  $^1\text{H}$  NMR. Three stable conformers, *ap*,  $\pm$ *sc*, and  $\mp$ *sc*, are possible and thus six conformers are drawn as in Scheme 2 if the two *m*-methyl groups are differentiated. Four modes of internal motions should be considered for the interconversion among the stable conformers: gear rotation in which the Ph group passes over a peri-hydrogen, GR(H), gear rotation in which the Ph group passes over the peri-substituent Y, GR(Y), isolated rotation at the *ap* site, IR(*ap*), and isolated rotation at the  $\pm$ *sc* sites, IR(*sc*).



Detailed dynamic  $^1\text{H}$  NMR study was made for 1-methoxy-9-(3,5-dimethylbenzyl)triptycene (**3**) as a typical peri-substituted derivative of **1** (ref. 7). Interconversion among the conformers is fast at ambient temperature but is frozen at  $-98^\circ\text{C}$ , where two unequally intense singlets were observed for the 1-methoxy protons, reflecting the presence of the *ap* and  $\pm$ *sc* conformers in a ratio of 3:7. The methylene signal is composed of a singlet due to *ap* and an

TABLE 3. Kinetic parameters for **3** and **4** by dynamic NMR.

Compd	<b>3</b>			<b>4</b>		
	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G_{200}^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G_{200}^\ddagger$
Process	kcal mol <sup>-1</sup>	cal mol <sup>-1</sup> K <sup>-1</sup>	kcal mol <sup>-1</sup>	kcal mol <sup>-1</sup>	cal mol <sup>-1</sup> K <sup>-1</sup>	kcal mol <sup>-1</sup>
GR(H) <sup>a</sup>	10.6 ± 0.1	-4.1 ± 0.5	11.5 ± 0.1			<7.7
GR(Y)			>12.7	11.8 ± 0.2	0.9 ± 0.7	12.0 ± 0.2
IR( <i>ap</i> )	9.6 ± 0.2	-3.1 ± 0.8	10.2 ± 0.1			>12.0
IR( <i>sc</i> )			>12.7			>>12.0

a) The kinetic parameters refer to the *ap*→*sc* process.

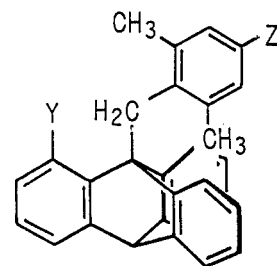
AB-quartet due to  $\pm sc$ , while two pairs of singlets are observed for the *m*-methyl protons. The lineshape of the methoxyl signal is controlled by the rate constant of the GR(H) process, that of the methylene signal depends on both GR(H) and GR(Y), and that of the *m*-methyl signal on all of GR(H), GR(Y), IR(ap), and IR(sc). Careful examinations of the spectra gave the kinetic parameters for GR(H) and IR(ap) as given in Table 3 and suggested that GR(Y) and IR(sc) have energy barriers at least 1.3 kcal mol<sup>-1</sup> higher than GR(H). Molecular mechanics calculations supported the experimental results.

In the oxygen counterpart, 1,4-dimethoxy-9-(3,5-dimethylphenoxy)tritycene (4), the 1-methoxyl signal remains a singlet throughout the temperature range studied, while the *m*-methyl signal splits into a pair of equally intense singlets at low temperatures (ref. 4). The results indicate that the GR(H) barrier is lower than 7.7 kcal mol<sup>-1</sup> and the lineshape change of the *m*-methyl signal is explained in terms of either GR(Y), IR(ap), or IR(sc) as the rate-determining step. Molecular mechanics calculations revealed that GR(Y) had the lowest barrier and therefore the observed dynamic NMR behavior was ascribed to GR(Y).

Therefore the slippage of the gear is a more favorable process than the meshed gearing in the methylene compound 3 while the meshed gearing is the lowest energy process in the oxygen compound 4.

### 9-(2,4,6-TRIMETHYLBENZYL)TRIPTYCENES

Introduction of two methyl groups into the *o*-positions of the Ph moiety of 1 is expected to destabilize the ground state and the IR transition state but not to significantly affect the GR transition state, rendering the meshed gearing the lowest energy process. The molecular mechanics calculation by Mislow et al. (ref. 6) indicated that GR is the lowest energy process in 9-(2,6-dimethylbenzyl)tritycene (5) and has the barrier of 4.9 kcal mol<sup>-1</sup>, which is too low to be detected by dynamic NMR. By introducing a peri-substituent Y, the GR(Y) process is expected to be observed by dynamic NMR. Actually dynamic <sup>1</sup>H NMR studies of several peri-substituted 9-(2,4,6-trimethylbenzyl)tritycenes (6) supported the expectation (ref. 3).



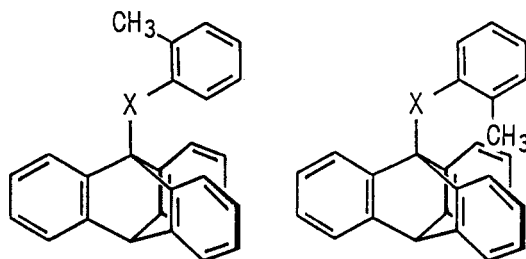
5 Y=Z=H  
6 Z=CH<sub>3</sub>

### 9-(2-METHYLBENZYL)TRIPTYCENE AND 9-(2-METHYLPHENOXY)TRIPTYCENE

9-(2-Methylbenzyl)tritycene (7a) and 9-(2-methylphenoxy)tritycene (7b) with a methyl group in one of the ortho positions of the phenyl group show interesting dynamic behavior. These compounds exist in a conformation in which the methyl group points outward as shown by the formula 9. Either the GR or IR process brings the molecule into a conformer 8 with the methyl group pointing inward. 8 is very unstable and immediately changes to a stable conformer 9 by another GR or IR (See Scheme 3 where Y=H).

In <sup>13</sup>C NMR spectra of 9, signals due to the aromatic carbons of the Tp moiety split into respective two peaks with an intensity ratio of 2:1 at low temperatures, while no lineshape change was observed for the Ph carbon signals. Lineshape analysis of the 4a/10a/11-C signal gave kinetic parameters given in Table 4 (ref. 5).

Interconversion among the stable conformers can occur either by two consecutive GR steps or by a combination of a GR step and an IR one. Since the NMR study did not tell the actual mechanism, molecular mechanics calculations were performed (Table 5). For both of 7a and 7b, conformers 8 with the methyl group pointing inward were calculated to be too unstable to be detected by NMR. The GR transition states were calculated to be lower in energy than the IR transition states and thus the conformer interconversion is



7a X=CH<sub>2</sub>  
b X=O

8

TABLE 4. Kinetic parameters for 7a and 7b by dynamic NMR.

Compd	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G_{250}^\ddagger$
	kcal mol <sup>-1</sup>	cal mol <sup>-1</sup> K <sup>-1</sup>	kcal mol <sup>-1</sup>
7a	10.7 ± 0.5	-4.4 ± 2.2	11.8
7b	9.5 ± 0.3	-4.5 ± 1.3	10.7

TABLE 5. Relative steric energies by molecular mechanics (kcal mol<sup>-1</sup>).<sup>a)</sup>

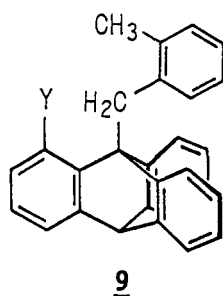
	7a	7b
GS CH <sub>3</sub> -out	0	0
CH <sub>3</sub> -in	6.84	8.62
TS GR	11.54	9.61
IR	16.00	20.03

a) by BIGSTRN-3/MM2.

suggested to occur by two GR steps. Actually the calculated GR barriers agree well with the observed ones. It is therefore concluded that both 7a and 7b behave as dynamic gears.

### PERI-SUBSTITUTED 9-(2-METHYLBENZYL)TRIPTYCENES

peri-Substituted derivatives of 7a and 7b show stereodynamically interesting behavior. As Scheme 3 shows, there exist three stable conformers, ap, +sc, and -sc, with the methyl group pointing outward, and the interconversion among them takes place by way of unstable conformers, ap', +sc', and -sc', with the methyl group pointing inward. Interconversion between +sc and -sc might occur by two consecutive GR(H) processes with ap' as an intermediate, while interconversion between ap and +sc (or -sc) can occur either by the process involving the GR(Y) step or by the one involving the IR(ap) step. The process involving the IR(sc) step would be neglected because IR(sc) is expected to have a far higher barrier than IR(ap).

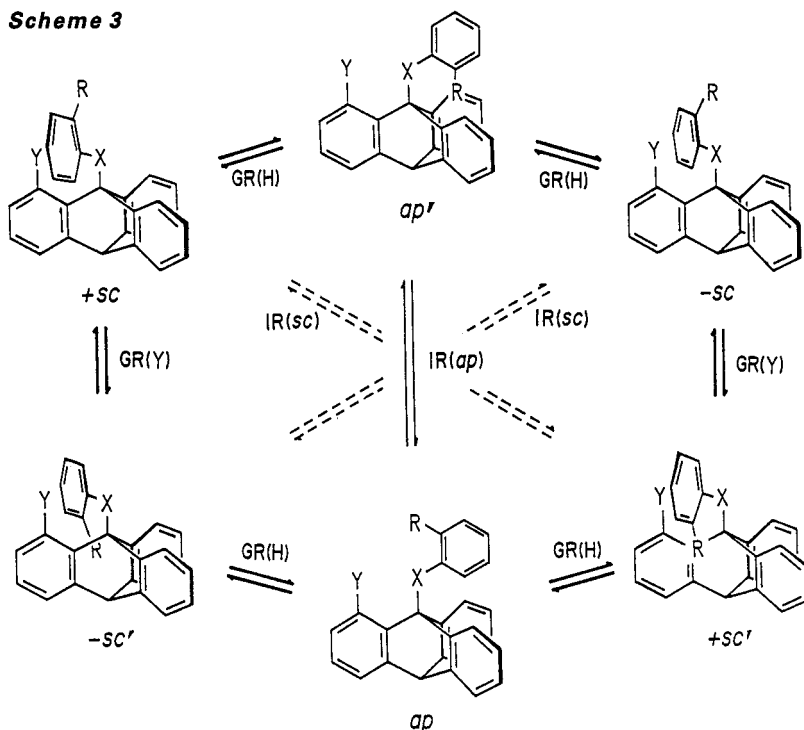
TABLE 6. Dynamic NMR data of 9.<sup>a)</sup>

Compd	Y	$\Delta G^\ddagger$ / kcal mol <sup>-1</sup> b)		$k_b$
		+sc $\rightleftharpoons$ -sc	ap $\rightleftharpoons$ $\pm$ sc	[ $\pm$ sc]/[ap]
9a	OCH <sub>3</sub>	13.2	17.7	2.9
9b	Cl	13.6	19.9	0.67
9c	Br	14.0	20.3	0.53
9d	CH <sub>3</sub>	13.9	19.6	1.0
9e	C $\equiv$ N	12.9	19.1	0.34
9f <sup>c)</sup>	C $\equiv$ CSi(CH <sub>3</sub> ) <sub>3</sub>	10.9 <sup>d)</sup>	18.1 <sup>d)</sup>	0.54 <sup>d)</sup>

a) Ref. 3. b) Values at the coalescence temperatures unless otherwise stated. c) Ref. 5. d) Values at 300 K.

Dynamic <sup>1</sup>H NMR of some peri-substituted 9-(2-methylbenzyl)tritypcene derivatives (9) has been studied (Table 5). The +sc  $\rightleftharpoons$  -sc interconversion monitored by the coalescence of the AB-quartet signal due to the methylene protons has a lower barrier than the ap  $\rightleftharpoons$   $\pm$ sc interconversion monitored by the lineshape change of the o-methyl signal, the methylene signal, and/or the peri-substituent signal (when Y=OCH<sub>3</sub> and CH<sub>3</sub>). The +sc  $\rightleftharpoons$  -sc barriers are rather insensitive to Y except for 9f. The steric interaction between Y and the eclipsing methylene hydrogen in the GR(H) transition state may be the main contributor to the peri-substituent effects in 9a-9e, and the large destabilization of the  $\pm$ sc ground state may be responsible for the low GR(H) barrier in 9f. As for the ap  $\rightleftharpoons$   $\pm$ sc processes, the compounds with a spherical and bulky peri-substituent, 9b-9d, have considerably higher barriers than 9a with a small methoxy group, while those with a cylindrical and tall peri-group, 9e and 9f have rather low barriers. The peri-substituent effect on the barrier in 9a-9d seems more compatible with the GR(Y) process rather than the IR(ap) process and a mechanism involving GR(Y) may operate in 9a-9d. Meanwhile a mechanism involving IR(ap) may operate when the peri-substituent is cylindrical and tall because the GR(Y) barrier would be very high in such compounds. Further studies are necessary for the elucidation of the actually occurring processes in these compounds.

Scheme 3



It has been our interest to isolate stable isomers due to restricted internal rotation. If both of the  $GR(Y)$  and  $IR$  barriers are higher than  $23 \text{ kcal mol}^{-1}$  in **9**, two isomers,  $ap$  and  $\pm sc$ , can be isolated as stable entities. If it is realized, this will be an example of residual isomerism and also a special case of phase isomerism (ref. 2). We at first expected that the isolation of isomers was realized in **9f**, where the  $GR(Y)$  barrier would be very high. The results showed that the  $IR(ap)$  barrier was rather low in **9f**. Molecular design to raise the  $IR$  barriers is necessary and the next choice may be oxygen analogs of **9f**, or 9-(2-methylphenoxy)tritypcenes with a cylindrical and tall peri-substituent and the study is in progress.

#### Acknowledgement

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